



2/4738

# FRANKLIN INSTITUTE LIBRARY

PHILADELPHIA

Class 667.3 Book C137D Accession 4738

ARTICLE V.—The Library shall be divided into TWO CLASSES; the first comprising such works as, from their rarity or value, should not be lent out, all unbound periodicals, and such text books as ought to be found in a library of reference, except when required by Committees of the Institute, or by Members or holders of second class stock, who have obtained the sanction of the Committee. The second class shall include those books intended for circulation.

ARTICLE VI.—The Secretary shall have authority to loan to Members and to holders of second class stock, any work belonging to the SECOND CLASS, subject to the following regulations :

*Section 1.*—No individual shall be permitted to have more than *two books* out at one time, without a written permission, signed by at least two members of the Library Committee; nor shall a book be ~~kept out~~ more than TWO WEEKS; but if no one has applied for it, the former borrower may renew the loan. Should any person have applied for it, the latter shall have the preference.

*Section 2.*—A FINE OF TEN CENTS PER WEEK shall be exacted for the detention of a book beyond the limited time; and if a book be not returned within three months, it shall be deemed lost, and the borrower shall, in addition to his fines, forfeit its value.

*Section 3.*—Should any book be returned injured, the borrower shall pay for the injury, or replace the book, as the Library Committee may direct; and if one or more books, belonging to a set or sets, be lost, the borrower shall replace them or make full restitution.

ARTICLE VII.—Any person removing from the Hall, without permission from the proper authorities, any book, newspaper, or other property in charge of the Library Committee, shall be reported to the Committee, who may inflict any fine not exceeding twenty-five dollars.

ARTICLE VIII.—No Member or holder of second class stock, whose annual contribution for the current year shall be unpaid, or who is in arrears for fines, shall be entitled to the privileges of the Library or Reading Room.

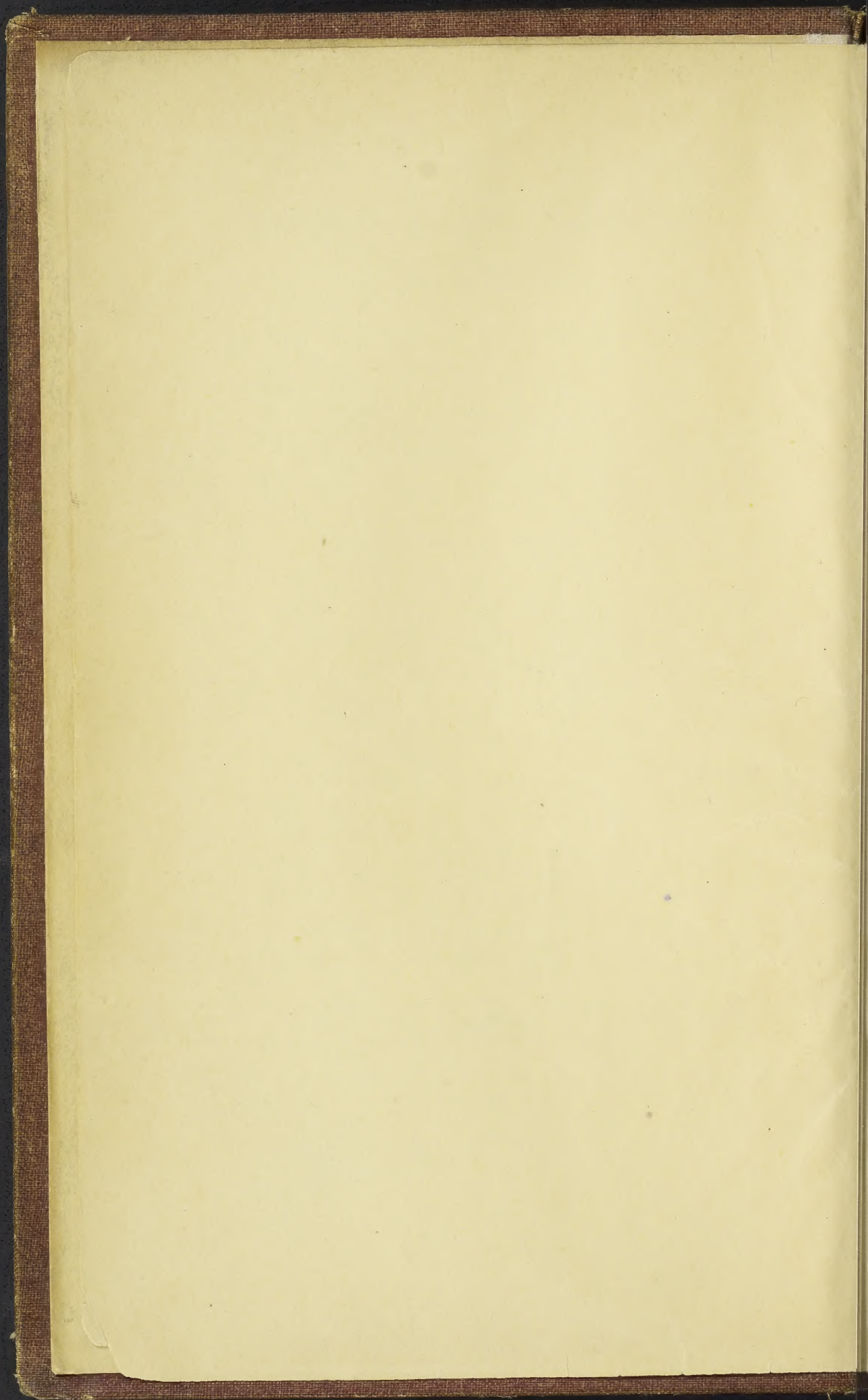
ARTICLE IX.—If any Member or holder of second class stock, shall refuse or neglect to comply with the foregoing rules, it shall be the duty of the Secretary to report him to the Committee on the Library.

ARTICLE X.—Any Member or holder of second class stock, detected in mutilating the newspapers, pamphlets or books belonging to the Institute, shall be deprived of his right of membership, and the name of the offender shall be made public.

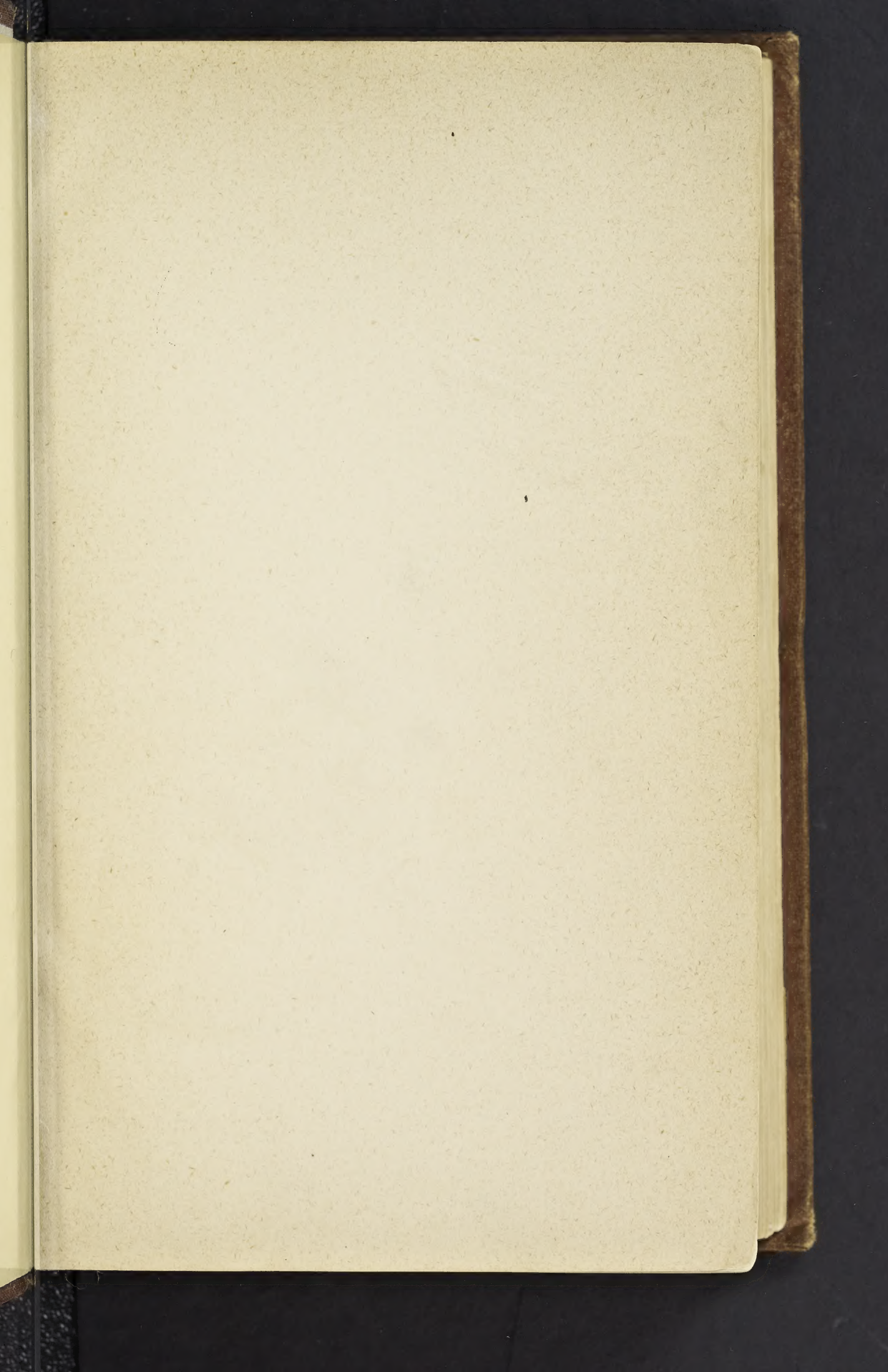




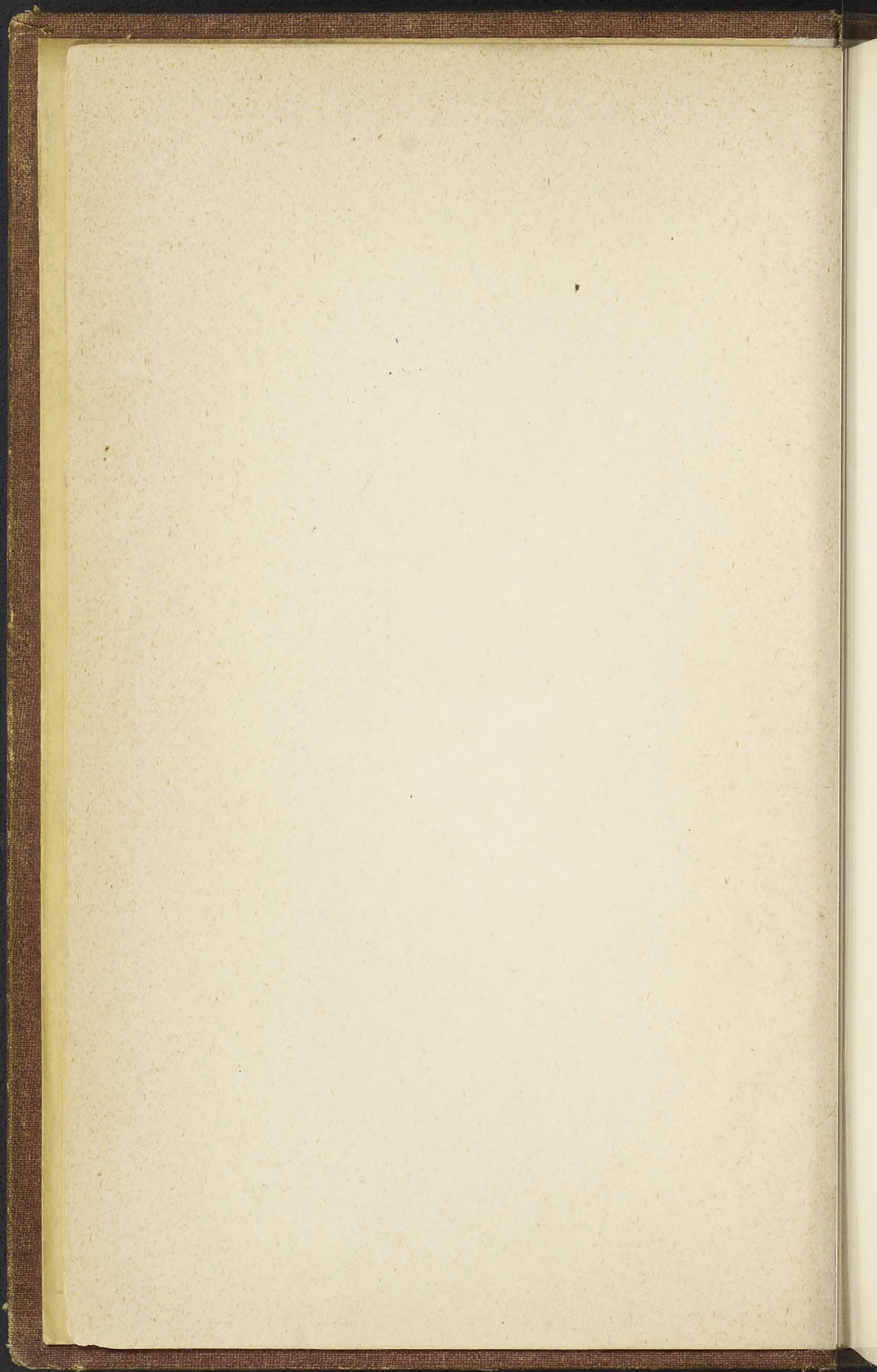
















DYEING AND CALICO PRINTING.



MANCHESTER:  
PALMER AND HOWE, PRINTERS, 1, 3, AND 5, BOND STREET.

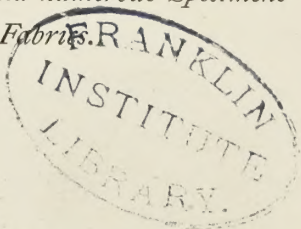


# DYEING AND CALICO PRINTING:

INCLUDING AN ACCOUNT OF THE MOST RECENT  
IMPROVEMENTS IN THE

*Manufacture and Use of Aniline Colours.*

*Illustrated with Wood Engravings and numerous Specimens  
of Printed and Dyed Fabrics.*



BY THE LATE

*DR. F. CRACE-CALVERT, F.R.S., F.C.S.,*

CORRESPONDING MEMBER OF THE ROYAL ACADEMY OF TURIN, OF THE  
MEDICAL SOCIETY OF BRUSSELS, THE INDUSTRIAL SOCIETY OF  
MULHOUSE, HONORARY MEMBER OF THE PHARMACEU-  
TICAL SOCIETIES OF LONDON AND PARIS, ETC.

EDITED BY

JOHN STENHOUSE, LL.D., F.R.S., &c.,

AND

CHARLES EDWARD GROVES,

*Fellow of the Chemical Societies of London and Berlin.*

MANCHESTER:

PALMER & HOWE, 1, 3, AND 5, BOND STREET.

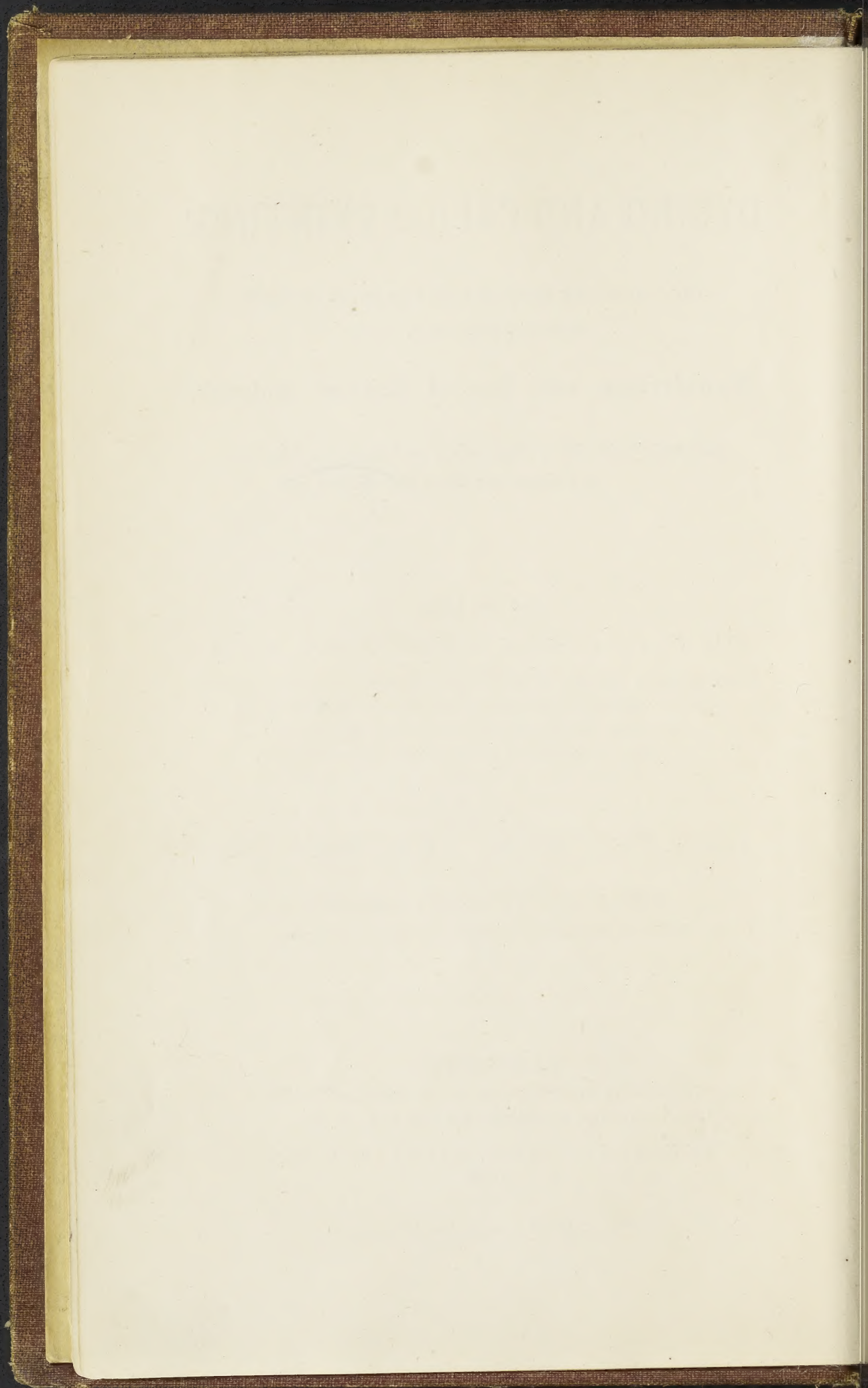
LONDON: SIMPKIN, MARSHALL, & CO.

NEW YORK: JOHN WILEY AND SON.

1876.

*The right of translation is reserved.*







## P R E F A C E.

---

THIS work, for the most part, consists of the revised MSS. of a treatise on colours other than aniline, on which the late Professor Crace-Calvert was engaged almost up to the time of his decease. The rapid strides which Chemical Science is now making, however, rendered numerous additions and corrections necessary so as to bring it, as far as possible, up to the present time; and, although the author did not contemplate treating of the Aniline Colours, yet from the great interest of the subject, both in its Theoretical and Technical aspect, it has been thought advisable to add a brief account of the most recent discoveries which have been made in this very important branch of the Colour Industry.

In a book like the present it would, of course, be impossible either to give a complete scientific account of the different chemical products connected with the various dyestuffs, or to enter into all the technical details of the Art of Dyeing and Calico Printing; the object of the late Professor Crace-Calvert being to present his readers with a general and comprehensive view of these important and interesting subjects.



In the alterations which we have made in the original MSS., and in the additions that have been found necessary, it has ever been our object to mould the work into the form in which, had he survived, the author himself would have wished to see it produced.

In conclusion, we have to thank those firms who have been kind enough to supply the Dyed and Printed Specimens with which to illustrate the work, viz., Messrs. Walter Crum and Co., Messrs. E. Potter and Co., Messrs. Salis Schwabe and Co., Messrs. Steiner and Co., Messrs. Symonds, Cunliffe, and Co., and Messrs. Wood and Wright, all of Manchester; Messrs. Heys and Co., of Barrhead, near Glasgow; Messrs. Marnas and Co., Lyons; Messrs. Dollfus, Mieg, and Co.; Mons. Gustave Schaeffer, of the firm Messrs. Haeffely and Co., Chateau de Pfstadt, near Mulhouse, who has given the specimens of coal-tar colours on woollen; and especially to Mons. Horace Koechlin, of Wesserling, Alsace, to whose courtesy and kindness we are indebted not only for the series of beautiful aniline colours printed on cotton, and for the new dyes Fluoresceïn, Coeruleïn, and Eosin, but also for several valuable epistolary communications.

*(Signed)*

JOHN STENHOUSE,  
CHARLES EDWARD GROVES.

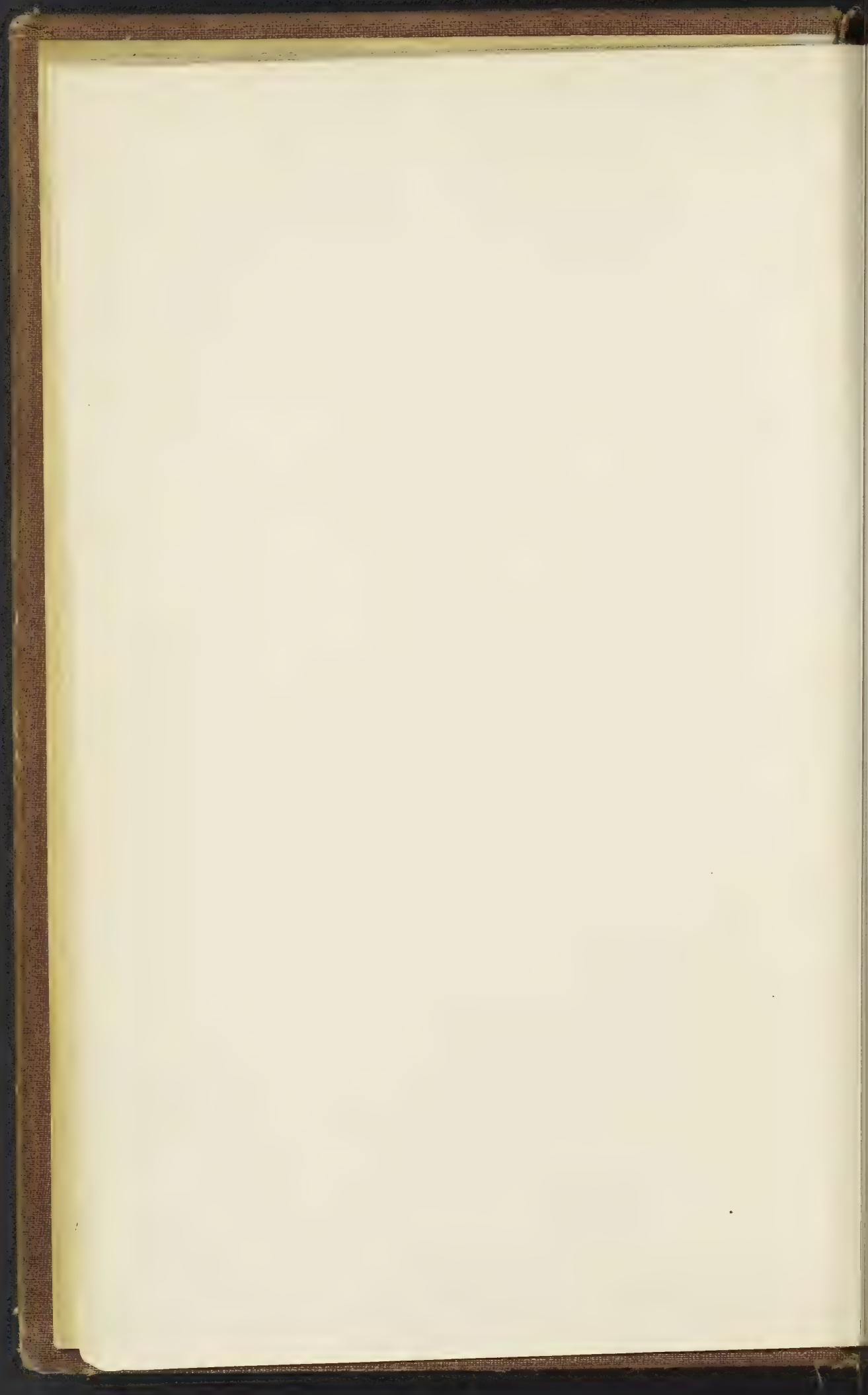
*London, 25th November, 1875.*





## OBITUARY.







## O B I T U A R Y

OF THE LATE

### DR. FREDERICK CRACE-CALVERT, F.R.S.

---

Dr. Frederick Crace-Calvert, F.R.S., was born near London on the 14th of November, 1819.

In the year 1835, when 16 years of age, he left London and went to France, where he commenced the study of chemistry under the celebrated chemist Gerardin, at Rouen, and continued with him for two years. At the expiration of this time he went to Paris, and carried on his studies at the Jardin des Plantes, the Sorbonne, Collège de France, and École de Médecine, his attention being principally given to the Natural Sciences.

About the age of 21 he was appointed to manage the well known works of Messrs. Robiquet & Pelletier, where the manufacture of pure chemicals and pharmaceutical products is carried on. This position, however, he soon vacated on being offered that of "Démonstrateur de Chimie Appliquée," under the eminent chemist Chevreul, and here he remained from 1841 till 1846, when he left France. From the former date his career as a chemist began; and was continued with untiring energy during the succeeding 32 years.

He published his first paper, "Sur l'extraction de quinine et cinchonine," in September, 1841.

In 1843, in conjunction with M. Ferrand, he elaborated an interesting paper on the analysis of gases enclosed in some organs



of plants, the gases being taken from the same plants at different times of the day and year in order to demonstrate the action of the sun's rays. This paper is entitled "*Memoir sur la Végétation*," and may be found in Volume V. of "*The Comptes Rendus*." In the following year the diseases of beer engaged his attention, and some interesting facts were embodied by him in a paper read to the *Société de Pharmacie*, "*Sur la fermentation visqueuse de la bière*."

From 1843 until the time of his leaving France he was engaged in a research on some compounds of lead which first brought him into note. One of the papers consequent on this may be found in the "*Comptes Rendus*" of 1843, entitled "*Procédé au moyen duquel on obtient un protoxyde de plomb cristallisé et ayant la couleur du minium*."

In 1844, he wrote "*On the presence of Indigo in the Orchidaceous plants*," in 1846, "*On the preparation of Calomel on the large scale*," and, in the same year, a compilation of facts relating to the properties of animal black.

On returning to England, at the latter end of 1846, he was first appointed to the chair of the honorary professorship of chemistry at the Royal Institution, and afterwards to that of lecturer on chemistry at the School of Medicine in Pine Street, Manchester.

In 1847, he published a paper "*On Bleaching Powders*," and, in 1848, one "*On the Bleaching of Cotton and Flax*."

About this time Dr. Calvert gave a long series of lectures on his favourite subject, at the Athenæum, Manchester, viz., "*The Application of Chemistry to Manufactures*." These were recorded in the daily papers.

During the following years many other subjects engaged his attention, but we may notice the following publications as some of the results of his labours.

In 1849 "*Process for the Preparation of Chlorates, particularly the Chlorate of Potash*."

In 1851 "*On the Oxides and Nitrates of Lead*."

In 1854 "*A case of Poisoning by the Sulphate of the Protoxide of Iron*."

In 1855 "*On the Adulteration of Tobacco*."—"On the Action



of Organic Acids on Cotton and Flax Fibres."—"On the Actions of Gallic and Tannic Acids in Dyeing and Tanning."

In 1856 "On the Solubility of Sulphate of Baryta in different Acids."—"On the Purification of Polluted Streams."

About this time he commenced an enquiry, in conjunction with Mr. Richard Johnson, on the physical and chemical properties of different alloys. The publications resulting from these investigations were:

In 1858 "On the Hardness of Metals and Alloys."—"On the Conductibility of Metals and Alloys."—"On the Chemical Changes which Pig Iron undergoes in its Conversion into Wrought Iron."

In 1861 a series of papers "On the Expansion of Metals and Alloys."

In 1862 "On the Composition of a Carbonaceous Substance existing in Grey Cast Iron."—"On the Employment of Galvanised Iron for Armour Plated Ships."—"On the Conductibility of Heat by Amalgams."

In 1863 "On the Preservation of Iron Plated and other Ships."

The interest he took in the preservation of ships from the action of sea water never ceased; many unrecorded experiments were carried on by him at intervals on this subject till the last days of his life.

In 1865 Mr. Richard Johnson and he published "On the Action of Sea Water on certain Metals and Alloys," and in 1866 "On the Action of Acids on Metals and Alloys."

In 1870, two papers appeared by Dr. Calvert, one "On the Composition of Iron Rust," the other "On the Oxidation of Iron," and a third on the same subject in 1871.

In 1858 we find a publication of his "On a New Method of preparing Hydrochloric Acid."

In 1859 "On the Analyses of Wheaten Flours."—"Influence of Science on the Arts of Calico Printing."—"On Starches: the purposes to which they are applied, and improvements in their Manufacture."

During this year, his attention was called by his friend the late Dr. Ransome to hospital gangrene, and in seeking its cause he was led to investigate the compounds produced during putrefaction.

Two papers, descriptive of his results, appeared in 1860, the first "On Products of Putrefaction." The second "On New Volatile Alkaloids given off during Putrefaction." He continued, these researches during the following two or three years, and had collected about an ounce of a precipitate, produced by combining the gaseous products of putrefaction with platinum, by passing the gases emitted by the putrefying meat through bichloride of platinum, by means of aspirators, during many months. This accumulation of precipitate was unfortunately destroyed before its examination could be completed, through the carelessness of one of his assistants, which caused him much regret ever afterwards.

In 1861 he wrote "On Improvements in the Manufacture of Colouring Matters," and "On the Chemical Composition of Steel." A report followed "On the Action of Water supplied by the Manchester Corporation on Lead of different kinds," in connection with the Manchester Sanitary Association.

In 1862 he gave a series of lectures to the Society of Arts, "On the Improvements and Progress in Dyeing and Calico Printing since 1851;" in 1864 "On Chemistry as applied to the Arts;" in 1866 "On Discoveries in Agricultural Chemistry," and "On Discoveries in the Chemistry of Rocks and Minerals."

These were the beginning of the Cantor lectures, which are now continued every year by different lecturers.

In this same year we find another paper by him, "On Wood for Shipbuilding."

In 1863 he patented and worked out his process for the separation of sulphur from coke, by the use of common salt, for the purpose of the manufacture of iron of superior quality.

The following is a list of some of his other publications:

In 1865 "On the Action of Silicate and Carbonate of Soda upon Cotton Fibres."—"On the Crystallised Hydrate of Phenic Alcohol."

In 1866 "On the Hydraulicity of Magnesian Limestone." "On the preparation of Acetylene."

About this time he interested himself with the properties of phenic or carbolic acid, and being satisfied of its valuable disinfecting properties, built works for its manufacture, and to him



belongs the honour of being the first to manufacture it in this country in a pure state; and through his exertions it has been introduced as a valuable therapeutic agent.

In 1867 he wrote papers "On Oxidation by means of Charcoal."—"On the Presence of Soluble Phosphates in Cotton Fibres, Wheat, and other Seeds," and five articles "On the Synthesis of Organic Substances."

In 1867 "Carbolic or Phenic Acid and its Properties" (three articles).

In 1869 "Presence of Soluble Phosphates in Seeds."—"Preparation of Nitrogen."

In 1870 "Testing Petroleum."

In 1872 "Sulphur in Coal and Coke;" and papers on "Protoplasmic Life;" "Vitality of Disease Germs," &c., which received much attention on the continent.

In 1873 he gave his last course of lectures in connection with his colleague the late Dr. Turner, at the Royal Institution, which were confined to physiology and the chemistry of the same, and in which both aimed to show that religion and science could go hand in hand, and neither produce injurious results on the other.

In concluding the list of Dr. Crace-Calvert's various researches we may mention that, besides the above, many others were made by him, but their unfinished state does not justify publication. Among these may be mentioned one on "Light," which cost him much labour, and one "On the Action of different Gases on each other under Enormous Pressures."

He was a Fellow of the Royal Society, of the Chemical Society, Member of Royal Academy of Turin, Member of Royal Academy of Medicine of Brussels, and of many other societies both at home and abroad.

Dr. Calvert showed remarkable devotion to the science he studied, and his knowledge of its literature was such as very few have attained, and such also as could only be obtained by a most unusual amount of reading, accompanied with strong interest, and in all probability much pleasure. He showed this knowledge more in the departments referring to industry, and, as might be

expected, he intended to give his experience to the public in a more convenient form than his lectures presented. One of these works relating to "Colours other than Aniline," was nearly completed before his last illness, and constitutes the first eleven chapters of the present volume. Whilst rather exhausted with this work, added to the attention required for the manufactures in which he was engaged, he was chosen as one of the Jury of the Vienna Exhibition. The summer of 1873 was sultry and unpleasant, and other causes may have operated to make it unhealthy; but whatever the reason or combination of reasons may have been (and we cannot doubt that his unceasing labours contributed), the result was that Dr. Calvert returned in a very enfeebled state, and a few days after his arrival in Manchester was seized with a fatal illness, which terminated on the 24th of October of the same year.

He was a firmly built man, of middle height, and apparently of unusual strength. He seemed to be younger in constitution than his years indicated. His manner was pleasing and animated, and he had great pleasure in communicating information. It is not attempted in this notice to say to what extent his writings have contributed to the advance of science, or the knowledge of manufactures, but in the latter department it is certain that his influence was widely felt, and his friendly disposition enabled him to become a frequent medium of communication between scientific men in England and in France, in both of which countries he felt equally at home. With these combined characteristics, the position he made for himself was peculiar, and of its importance we may judge partly by the fact that, although one to which many would be glad to attain, it is not yet filled up; and, as Dr. Angus Smith remarked at the Manchester Philosophical Society, "his death was regretted not only by those who knew him as a chemist, but also by those who but knew him as a man."



FRANKFURT

## CONTENTS.

---

### CHAPTER I.

|   | PAGE. |
|---|-------|
| INTRODUCTORY .....  | I     |
| Natural Colours; Cause of Colours, 1.—Analysis of White Light; the Spectrum, 2.—Nature of Colouring Matters, 3.—Action of Light on Colouring Matters, 6.—Colouring Matters of Flowers; Cyanin, 7.—Xanthin, 8.—Xanthein: Reducing Power of the Roots of Plants, 9.—Action of Electricity on the Colouring Matters of Flowers, 10.—Action of Heat on Colouring Matters, 11.—Action of Chlorine on Colouring Matters, 12.—Action of Hypochlorites on Colouring Matters: Decolourising Power of Charcoal, 13.—Animal Charcoal: Solubility of Colouring Matters; 14.—Bleaching Action of Sulphurous Acid: Compounds of Metallic Oxides with Colouring Matters; Lakes, 16.—Theory of Mordants; Thom's Experiments on Mordants, 17.—Oxidising Effect of certain Salts on Colouring Matters, 18.—'Fast' and 'Loose' Colours, 19.—Effect of Heat and Light on the Colours of Dyed Fabrics, 20. |       |

### CHAPTER II.

|   |    |
|---|----|
| MADDER .....  | 22 |
| The Madder Plant, 22.—Madder Root; Preparation of Madder; Composition of Madder, 23.—Avignon Madders, 'Paluds' and Rosées: Erythrozym: Rubian, 24.— |    |

Kuhlmann's Xanthin, 25.—Action of Erythrozym, of Acids, and of Alkalis on Rubian, 29.—Formation of Alizarin from Rubian, 31.—Verantin, 32.—Rubiretin, Rubianin, Rubiacic Acid, 33.—Rubiacin, 34.—Sugar in Madder: Ruberythic Acid; Decomposition of Ruberythic Acid into Alizarin and Sugar, 35.—Isalizarin, Hydralizarin, and Pseudopurpurin, 36.—Purpuroxanthin, 37.—Preparation and Properties of Alizarin, 38.—Conversion into Anthracene: Nitroalizarin, 41.—Amidoalizarin, 42.—Alizarinamide, 43.—Anthraflavic Acid, 44.—Anthrapurpurin, 45.—Manufacture of Anthracene, Properties of Anthracene, 46.—Conversion into Anthraquinone, Preparation of Artificial Alizarin, 48.—Caro, Graebe, and Liebermann's Patent, 50.—Broenner and Gutzkon's Patent, 54.—Anthracene Orange: Naphthazarin, 55.—Oxynaphthalic Acid, 56.—Purpurin and its Derivatives, 58.—Optical Properties of Purpurin and Alizarin, 60.—Detection of Purpurin and Alizarin, 62.

## CHAPTER III.

MADDER.—*Continued* ..... 64  
 Use of Madder, 64.—Turkey or Adrianople Red, Historical, 65.—Processes for producing Turkey Red, Oiling the Cloth, 66.—Mordanting the Cloth, Dyeing the Cloth, 67.—Clearing the Dyed Cloth, 68.—Effect of Oiling, 69.—Persoz' Explanation, 70.—Printing Turkey Red, Müller's Process, 71.—Calico Printing, Mordants Employed, 72.—Recipes for Mordants for various Colours, 73.—Method of Printing Mordants, 76.—Ageing; Thom's Process, 77.—Dunging, 78.—Construction of Dyebeck, 79.—Method of Dyeing with Madder; Use of Chalk in Madder Dyeing, 81.—Soaping and Clearing Madder-Dyed Goods, 83.—Manufacture of Garancin, 84.—'Garancine Modifiée?' Utilisation of Waste Products, 85.—Dyeing Power of Garancin, 86.—Advantages of Garancin over Madder:



# CONTENTS.

xvii.

PAGE.

'Commercial Alizarin,' 87.—Garanceaux: *Fleurs de Garance*, or Flowers of Madder, 88.—Alcohol from Madder Washings, 89.—Madder Extracts, 90.—Leitenberger's Extract, 91.—Paraf's Extract: Kopp's Purpurin and Green Alizarin, and Dyestuffs obtained from them, 92.—Pernod's Extract, 95.—Rien's Process for Extracting Alizarin and Purpurin: Recipes for Dyeing with Madder Extracts, 96.—Table of Colours obtained by Printing a Mixture of Madder Extract with the Acetates of various metals, 98.—Printing with Artificial Alizarin, 100.—Recovery of Waste Colours; Scheurer's Process, 101.—Koechlin's Process for the Recovery of Waste Colour, 102.—Thom and Stenhouse's Process for the Utilisation of Soap Waste: Manufacture of Madder Lakes, 103.—Adulteration of Madder, 104.—Testing the value of Madder, &c., 105.—Testing Madder-Dyed Fabrics, 107.—Munjeet, 108.—Munjistin, 109.—Chayaver, 110.—Al' Root, or Sooranjee (*Morinda Citrifolia*), Morindin and Morindone, 111.

## CHAPTER IV.

RED DYEWOODS, SAFFLOWER, ALKANET ..... 113

Red Dyewoods, Campeachy or Logwood, 113.—Hæmatoxylin, 114.—Hæmatein, 115.—Reactions of Hæmatoxylin, 117.—Preparation of Logwood, 118.—Extract of Logwood; Dyeing Purple with Logwood, 119.—Logwood Black, 120.—Brazil Wood, and Peach Wood or Santa Martha Wood, 121.—Sapan Wood; Lima Wood; The Colour-giving principle of these Woods, 122.—Brazilin, and its Relation to Hæmatoxylin, 123.—Brazilein, 124.—Reactions of the Brazil Wood Group: Extracts of Brazil and Sapan Woods, 125.—Dingler's Process; Dyeing with Brazil Wood Extract, 126.—Pink Lakes—Venetian Lake: Sandal Wood, Barwood, and Camwood or Kambe Wood, 128.—Colouring principle of Sandal Wood, 129.—Mock Turkey Red, 131.—Re-

actions of Sandal Wood and Barwood, 132.—Sorgho, 133.—Sorgho Carmine or Sorgho Red; Alkanet; Anchusin, 134.—Cenolin, the Colouring principle of Wines: Safflower, 135.—Preparation of Safflower: Composition of Safflower, 136.—Carthamin, 137.—Yellow Colouring Matter of Safflower: Dyeing with Safflower, 138.

## CHAPTER V.

|  |     |
|--|-----|
| INDIGO .....   | 140 |
| History of Indigo: Plants which furnish Indigo, 140.—  |     |
| Manufacture of Indigo, 141.—Woad or Pastel, 143.—  |     |
| Tein hoa tein ching ( <i>Isatis Indigotica</i> ): <i>Polygonum tinctorium</i> , 144.—Colouring principle of the Indigoferæ, 144.—  |     |
| Indican, Schunck's Researches, 146.—Schunck's Apparatus for Evaporation, 147.—Action of Acids on Indican, 150.—Indirubin, 151.—Indiretin, Indihumin, and Indiglucin, 153.—Action of Alkalis on Indican; Indicanin, 155.—Oxindicanin, 157.—Pure Indigotin, 158.—  |     |
| Isatin, 159.—Isatic Acid; Isatyde, 160.—Sulphisatyde and Disulphisatyde: Indin and its Derivatives: Compounds obtained with Isatin and Ammonia, 161.—Action of Hydriodic Acid on Isatin; Isatopurpurin and Isatoflavin: Indigotic or Nitrosalicylic Acid, 162.—Picric Acid from Indigo, 163.—Action of Chlorine on Indigo, 164.—Chlorisatin, and Dichlorisatin, 165.—Chloranil or Perchlorquinone: Bromisatins, 166.—Chrysanilic Acid: Anthranilic or Phenylcarbamic Acid, 167.— |     |
| Aniline from Indigo: Synthesis of Indigo, 169.—Dioxindol or Hydrindic Acid, 170.—Oxindol, and Indol, 171.—Baeyer and Emmerling's Experiments on the Reduction of Isatin, 173.  |     |

## CHAPTER VI.

|   |     |
|---|-----|
| INDIGO— <i>Continued</i> .....                    | 175 |
| Indigosulphonic Acids; Sulphopurpuric Acid, 175.— |     |



# CONTENTS.

xix.

PAGE.

Sulphindigotic Acid, 176.—Hypósulphindigotic Acid, 177.—Saxony Blue, and Indigo Carmine, 178.—Bailey's Indigo Carmine, 179.—Action of Alkalis on the Indigo-sulphonic Acids; Sulphoviridic Acid, 180.—Sulphorufic Acid, and Sulphopurpuric Acid, 181.—White or Reduced Indigo; Dumas' Process for Preparing White Indigo, 182.—Schützenberger and Lalande's Process, 184.—Lightfoot's Process for Chintzes, 186.—Schlumberger's Process: Steam Style: Purification of Indigo, 188.—Characters of Bengal Indigo, 189.—Chevreul's Analysis of Indigo: Testing Indigo, 191.—Cold Vat: Recovery of Waste Indigo, 197.—Pulverisation of Indigo, 198.—Cohen's Process for Cold Vat, 199.—Resist or Reserve Process, 200.—Discharge Process, 201.—China Blue: Indian Vat for Dyeing Wool, 203.—Leuch's Vat, 204.—Formation of Indigo in the Human System, 205.

## CHAPTER VII.

|  |     |
|--|-----|
| COCHINEAL, KERMES, GUM-LAC, LAC DYE, LAC LAKE, AND MUREXIDE .....  | 206 |
| History of Cochineal, 206.—Preparation of Cochineal, 207.—Composition of Cochineal according to John: Preparation of Carminic Acid, 209.—Carmine red, 211.—Properties of Carmine Acid, 212.—Nitrococcusic Acid: Reactions of Cochineal, 213.—Adulteration of Cochineal, and Testing Cochineal, 214.—Dyeing with Cochineal, 216.—Ammoniacal Cochineal, and Carminamide: Carmine Lakes, 218.—Preparation of 'Carmine,' 219.—Florentine Lake: Kermes, 220.—Uses of Kermes, 221.—Stick Lac, 222.—Composition of Stick Lac; Seed Lac, 223.—Composition of Seed Lac; Shell Lac; Composition of Shell Lac; Lac Lake, 224.—Composition of Lac Lake; Lac Dye; Brooke's Lac Dye: History of Murexide, 225.—Preparation of Murexide, 226. |     |

## CHAPTER VIII.

|  |     |
|--|-----|
| ORCHIL, CUDBEAR, AND LITMUS.....   | 228 |
| Discovery of Orchil: Nature of Lichens, 228.—Species of Lichens used for the Preparation of Orchil, and Manufacture of Orchil, 229.—French Purple, 232.—Process for Testing Lichens: Uses of Orchil: Discovery of Orcin, 233.—Preparation of Orcin and Erythrite, 234.—Properties of Orcin, 235.—Haloïd Derivatives of Orcin: Nitro Derivatives of Orcin, 236.—Orceïn, 237.—Methyl, Ethyl, and Amyl Orcins, 238.—Erythrin or Erythric Acid, 239.—Picroerythrin: Lecanoric Acid, or Lecanorin, 240.—Properties of Lecanoric Acid, 241.—Ethylic Orsellinate: Preparation of Picroerythrin, 242.—Properties of Picroerythrin: Erythrite or Erythromannite, 243.—Tetranitroerythrite: Usnic acid, 244.—Evernic Acid, and Everninic Acid: Cladonic Acid, or $\beta$ -usnic Acid, 245.—Orsellinic Acid, or Orsellesic Acid, 246.—Other Compounds obtained from the Lichens: Summary: Cudbear, 247.—Litmus, or Lacmus, 248.—Tournesol: Resorcin, 249.—Azoresorcin Derivatives, 250.—‘Eosin,’ or Tetrabromofluoresceïn, 251. |     |

## CHAPTER IX.

|  |     |
|--|-----|
| QUERCITRON, FUSTIC, PERSIAN BERRIES, WELD, ALOES, TURMERIC, ANNATTO, ILIXANTHIN, &C., LO-KAO...  | 253 |
| Quercitron, 253.—Reactions of Quercitron Bark, 254.—Quercitrin: Decomposition of Quercitrin by Acids, 255.—Isodulcite, and Quercetin, 256.—Action of Potassium Hydrate on Quercetin, 257.—Quercetic Acid, Quercimeric acid, and Paradatiscetin, 258.—Phloroglucin: Reducing Action of Sodium Amalgam on Quercetin, 259.—Flavin, 260.—Dyeing with Quercitron Bark and Flavin, 261.—Old Fustic, 262.—Reactions of Old Fustic; Colouring Matters of the Wood, 263.—Morintannic Acid, or Maclurin, 264.—Machromin, 265.— |     |



Moric Acid, or Morin, 266.—Analogy between Quercetin and Morin, 267.—Dyeing with Old Fustic: Young Fustic, 268.—Fustin: Reactions of Young Fustic, 269.—Dyeing with Young Fustic: Persian Berries, whence obtained; Reactions of Persian Berries, 270.—Kane's Chrysorhamnin and Xanthorhamnin; Results of Gelatly's Investigations, 271.—Observations of Hlasiwetz, Bolley, Schützenberger, and Bertéche; Lefort's Rhamnagin and Rhamnin, 272.—Summary of Results, 273.—Melin from Waifa: Dyeing with Persian Berries, 274.—Dutch Yellow, 275.—Weld; Reactions of Weld, 276.—Luteolin, 277.—Use of Weld: Source of Aloes, 278.—Socotrin or Bombay Aloes, Barbadoes Aloes, Natal Aloes, and Cape Aloes, 279.—Preparation of Barbaloin, 280.—Haloid Derivatives of Barbaloin: Nataloin, and Socaloin, 281.—Aloetic Acid, 282.—Chrysammic Acid, 283.—Hydrochrysammide: Colours obtained with Aloes: Turmeric, 284.—Composition of Turmeric: Curcumin, 285.—Rosocyanin: Dyeing with Turmeric, 287.—Preparation and Composition of Annatto, 288.—Testing Annatto, 289.—Colouring Matters of Annatto; Orellin and Bixin, 290.—Uses of Annatto: Chica, or Carajara, 291.—Saffron; Crocin: Barberry Root, 292.—Berberine and its Sources, 293.—Gamboge, 294.—Composition of Gamboge, 295.—Ilixanthin: Yellow Colouring Matters from Lichens, 296.—Purree, or Indian Yellow; Euxanthic Acid, 297.—Euxanthone: Rhubarb; Chrysophanic Acid: Rutin, 298.—Scoparin, 299.—Taigu, or Tayegu Wood; Tayguic Acid, 300.—Wongshy, or Hoang-tchy: Carotin, &c.: Rottlerin: Lo-kao, or Chinese Green, 301.—Lokain, 303.—Lokaetin, 304.—Sap Green, or Bladder Green: Preparation of Chlorophyll, 305.—Fremy's Phylloxanthin, and Phyllocyanin, 307.—Stokes' Examination of Chlorophyll, 308.—Lommel's Observations: Xylochloric Acid: Printing Chlorophyll, 309.

## CHAPTER X.

|   |     |
|---|-----|
| TANNIN MATTERS.....                                     | 310 |
| Nature of Tannin Matters, 310.—Two Classes of Tannins:  |     |
| Preparation of Tannic or Gallotannic Acid, 311.—        |     |
| Decomposition of Tannin by Heat: Schiff's Researches    |     |
| on Tannin, 312.—Digallic Acid: Tannoxylic or Ruffi-     |     |
| tannic Acid: Gallic Acid, 313.—Preparation and Pro-     |     |
| perties of Gallic Acid, 314.—Ruffigallic Acid, 315.—    |     |
| Decomposition of Gallic Acid by Heat; Preparation       |     |
| of Pyrogallic Acid, or Pyrogallol, 316.—Galleïn, and    |     |
| Gallin, 318.—Coeruleïn, 319.—Coërolin, 320.—Ellagic     |     |
| Acid: Mode of Formation of Gall-nuts, 321.—Com-         |     |
| position of Gall-nuts: Reactions of a Solution of Gall- |     |
| nuts, 322.—Knoppers: Chinese Galls, or Japanese         |     |
| Galls, 323.—Valonia, 324.—Cultivation of Sumach;        |     |
| Reactions of a Decoction of Sumach, 325.—Uses of        |     |
| Sumach, 326.—Bablah, Babool, or Neb-neb, 327.—          |     |
| Chesnut Bark, Dividivi, Myrobalans, Oak Bark, and       |     |
| Spruce Bark or Hemlock Tree Bark, 328.—Compounds        |     |
| obtained from Walnut Husks: Hennis, 329.—Prepara-       |     |
| tion of Catechu: Source of Gambier: Kino, or 'Gum       |     |
| Kino,' 330.—Bombay, Bengal, and Gambier Catechu,        |     |
| 331.—Reactions of Catechu; Adulteration of Catechu,     |     |
| 332.—Catechutannic Acid, 333.—Catechin, or              |     |
| Catechuic Acid, 334.—Products of the Decomposition      |     |
| of Catechin, 335.—Pyrocatechin, 336.—Dyeing and         |     |
| Printing with Catechu; Catechu Browns, 337.—            |     |
| Estimation of Tannin, 338.—Amount of Tannin in          |     |
| various Vegetable Substances, 340.                      |     |

## CHAPTER XI.

|  |     |
|--|-----|
| ON THE EXAMINATION OF COLOURING MATTERS AND          |     |
| COLOURED FABRICS .....                               | 342 |
| Uses of the Colorometer, 242.—Houton-Labillardière's |     |
| Colorometer, 343.—Collardeau's Colorometer, and Du-  |     |



bosc and Mene's Colorometer, 344.—Wilson's Colorometer, 345.—Spectroscopic Examination of Colours, 346.—Use of Oxidising Agents: Comparison of the Dyeing Powers of Dyestuffs, 347.—Adulteration of Dyestuffs, 348.

## CHAPTER XII.

## BENZENE, ANILINE, AND MAGENTA..... 350

Constituents of Coal-tar, 350.—Historical Account of Aniline, 351.—Distillation of Coal-tar, and Extraction of Aniline from Coal-oil, 352.—Preparation of Benzene from Light Oil, 353.—Benzene from Benzoic Acid; Properties of Benzene, 354.—Manufacture of Nitrobenzene, 355.—Dinitrobenzene: Preparation of Aniline from Nitrobenzene, 356.—Manufacture of Aniline, 357.—Properties of Aniline, 358.—Formation of Magenta: Toluene, 359.—Nitrotoluenes, 360.—Toluidines: Commercial Aniline, 362.—Historical Account of Magenta, 363.—Manufacture of Magenta, 365.—Purification of Magenta, 367.—Rosaniline, 368.—Salts of Rosaniline, 369.—Leucaniline: Hydrocyanrosaniline, 370.—Manufacture of Rosaniline, and of Rosaniline Acetate, 371.—Caro and Dale's Process for Magenta, Laurent and Casthelaz Process, 372.—Coupier's Process: Rosotoluidine, or Toluidine Red, 373.—Xylidine Red: Pararosaniline: Dyeing with Magenta, 374.—Printing Silk and Wool with Magenta, Dyeing Cotton and Mixed Fabrics with Magenta, 377.—Printing Cotton with Magenta: Magenta Purple, 378.—Adulteration of Magenta, 379.—Safranine, or Saffranine, 380.—Geranosine, Ponceau, and Cerise, 382.—Ulrich's Scarlet, 383.

## CHAPTER XIII.

## ANILINE VIOLETS AND ANILINE BLUES ..... 384

Aniline Violets: Discovery of Mauve, 384.—Manufacture

of Mauve, 385.—Mauveine, 386.—Phoenicine, 387.—Runge's Blue: Various Processes for obtaining Mauve, 388.—'Violet Imperial,' Monophenylosaniline, 390.—Diphenylosaniline: 'Regina Purple,' 391.—Kopp's Violet: Mauvaniline and Violaniline, 392.—Methyl and Ethyl Rosanilines, 393.—Manufacture of Hofmann Violet, 395.—Ethylmauveine or 'Dahlia,' 396.—Manufacture of Methylaniline, and Paris Violet, 397.—Methylaniline and Ethylaniline from 'Hofmann Gum:' 'Dorothea Violet,' 398.—Benzyl Chloride: Violets from Tertiary Monamines, 399.—'Britannia Violet:' Aldehyde Violet: Dyeing with Aniline Violets, 400.—Dale's Recipes for Printing, 401.—Aniline Blues; 'Bleu de Paris,' and 'Bleu de Mulhouse,' 402.—Manufacture of 'Bleu de Lyon,' 403.—Purification of 'Bleu de Lyon,' 'Bleu Lumière' or 'Night Blue,' 404.—Bardy's Process for Aniline Blue and Violet, 405.—Difference between 'Bleu de Paris' and 'Bleu de Lyon,' 406.—Nicholson's Soluble Blue, 407.—Toluidine Blue, 408.—Manufacture of Diphenylamine, 409.—Diphenylamine Blue, 410.—Azodiphenyl Blue: Dyeing with Aniline Blue, 411.

## CHAPTER XIV.

|   |     |
|---|-----|
| ANILINE GREEN.—ANILINE YELLOW .....   | 414 |
| Emeraldine: Discovery and Preparation of Aldehyde Green, 414.—Historical Account of Iodine Green, 416.—Wanklyn's Process; Hofmann and Girard's Process, 417.—Manufacture of Iodine Green, 418.—Soluble Green, and Crystallised Green, 420.—Transformation of Iodine Green, 421.—Perkin's Green, and Methyl Green, or Methylaniline Green, 422.—Dyeing with Aniline Greens, 423.—Aniline Yellows; Chrysaniline, or Phosphine, 425.—Chrysotoluidine; Purification of Chrysotoluidine, 426.—Preparation of Chrysotoluidine from Toluidine; Properties of Pure Chrysotoluidine, 428.—Scheurer-Kestner's Orange: Diazoamidobenzene |     |



and Amidodiphenylimide, 429. — Vogel's Zinaline: Adulteration of Aniline Yellow, 430.

## CHAPTER XV.

## ANILINE BROWNS AND ANILINE BLACK ..... 432

Aniline Maroons and Browns: Girard and De Laire's Maroon: Schultz' Garnet, 432.—Jacobsen's Browns; Koechlin's Brown, 433.—Wise's Brown, and Sieberg's Brown, 434.—Dyeing with Aniline Brown: Aniline Black, 435.—Lightfoot's Processes, 436.—Lauth's Process, 437.—Koechlin's Recipe, 438.—Sacc's Recipe for Olive Browns: Dullo's Black: Lauth's Manganese Mordant, 439.—Spirk's Recipes, 440.—Aniline Black with Albumen: Jarossen and Muller's Process: Schlumberger's Process, 441.—Nature of Aniline Black, 442.—Lightfoot's Experiments, 443.—Rheineck's Experiments; Nigraniline, 444.—Qualities of Aniline adapted for Aniline Black, 445.—Process for Aniline Black with Potassium Dichromate, 446.—Aniline Black on Wool: Läubler's Aniline Grey, 448.—Casthelaz Grey, 449.

## CHAPTER XVI.

## PHENOL, CRESOL, AND NAPHTHALENE COLOURS ..... 450

Phenol or Carbolic Acid, 450.—Picric Acid or Trinitophenol; Manufacture of Picric Acid, 452.—Properties of Picric Acid; Dyeing with Picric Acid, 454.—Picric Acid as a Test for Cotton in Mixed Fibres: Adulteration of Picric Acid, 455.—Picramic Acid or Dinitroamidophenol: Isopurpuric Acid, 456.—Difference between Murexide and Isopurpuric Acid, 457.—Dyeing with Isopurpurates: Rosolic Acid, 458.—Manufacture of Corallin, 459.—Crystalline Corallin: Formation of Corallin, 460.—Printing with Corallin, 461.—Peonine or Red Corallin, 462.—Dyeing and Printing with Peonine and Corallin, 463.—Azulin, 464.—Pseudocorallin, 465.—Aurin, 466.—Leukaurin, 467.—Printing

with Aurin: Phenicienne or Rothine: Fol's Yellow, 468.  
 —'Campo Bello Yellow:' Cresol Colours: Gold Yellow,  
 469.—Victoria Yellow: Naphthalene Colours: Naphtha-  
 lene, 470.—Dinitronaphthol, 471.—Manchester Yellow  
 or 'Martius' Yellow,' 472.—Naphthylpurpuric Acid, and  
 Indophane: Resorcin Indophane, 473.—Chloroxy-  
 naphthalic Acid, 474.—Carminaphtha: Nitroxynaph-  
 thalic Acid or 'French Yellow:' Naphthylamine, 475.  
 —Preparation of Nitronaphthalene, and Manufacture of  
 Naphthylamine, 476. — Azodinaphthyldiamine, 477.—  
 Rosanaphthylamine or 'Magdala Red,' 478.—Naph-  
 thylamine Violet, 479.—Ballò's Violet, 480.

---

## A P P E N D I X.

|  |     |
|--|-----|
| TABLES FOR DISTINGUISHING THE DIFFERENT COLOURING<br>MATTERS FIXED ON TISSUES BY PRINTING OR<br>DYEING .....   | 481 |
| Blue Colouring Matters, including—Vat Indigo, Indigo<br>Carmine, Alkaline Sulphindigotates, Saxony Blue,<br>Prussian Blue, Logwood Blue, Aniline Blue, and Ultra-<br>marine, 482.—Yellow Colouring Matters, including—<br>Quercitron, Persian Berries, Old Fustic, Weld, Barberry<br>Root, Turmeric, Annatto, Picric Acid, Chrome Yellows,<br>Ochre and Orpiment, 484.—Red Colouring Matters,<br>including—Cochineal, Brazil Wood, Madder Reds,<br>Safflower, Murexide, and Aniline Reds, 486.—Green<br>Colouring Matters, including—1, Indigo Blue, and a<br>Vegetable Yellow; 2, Logwood Blue, and a Vegetable<br>Yellow; 3, Lokao; 4, Aniline Green; 5, Aniline Blue<br>and Picric Acid, or Vegetable Yellow; 6, Scheele's<br>Green; 7, Oxide of Chromium, 488.—Purple Colours,<br>including—Mauve, Aniline Purple, Hofmann's Aniline<br>Violet, Madder Purples, Alkanet, Orchil, and Logwood |     |



# CONTENTS.

xxvii.

PAGE.

Purple, 490.—Brown Colours, including—Madder, Catechu, Browns produced with Red Dyewoods, Manganese, and the Brown produced by the employment of Blue, Yellow, and Red on Woollen, 492.—Black and Grey Colours, including—Logwood with Iron Mordant, Tannin, Chrome Black, Madder Black, Black with Bottom or Ground of Vat Indigo, and Aniline Black, 494.

|  |     |
|--|-----|
| TABLE OF PROPERTIES AND REACTIONS OF VARIOUS COM-<br>POUNDS OBTAINED FROM MADDER ..... | 496 |
|--|-----|

## LIST OF PRINTED AND DYED PATTERNS.

|  | PAGE. |
|--|-------|
| Turkey red as dyed, Messrs. Steiner and Co. ....                                       | 68    |
| „ after first clearing, Messrs. Steiner and Co. ....                                   | 68    |
| „ finished, Messrs. Steiner and Co. ....   | 69    |
| Madder purple, Messrs. Symonds, Cunliffe, and Co. ....                                 | 74    |
| Madder red and pink, Messrs. Symonds, Cunliffe, and Co. ....                           | 75    |
| Effect produced by a six-colour machine, Messrs. Walter Crum and Co. .                 | 77    |
| Madder style, mordanted cloth, Messrs. Symonds, Cunliffe, and Co. ....                 | 79    |
| „ after dyeing, Messrs. Symonds, Cunliffe, and Co. ....                                | 83    |
| „ cleared, Messrs. Symonds, Cunliffe, and Co. ....                                     | 83    |
| Garancin style, Messrs. Wood and Wright.....   | 87    |
| Pincoffine, or 'commercial alizarin,' Messrs. Salis Schwabe and Co. ....               | 88    |
| Orange extract of madder: red, Messrs. Dollfus, Meig, and Co.....                      | 95    |
| „ „ purple, Messrs. Dollfus, Meig, and Co.....   | 95    |
| Extract of garancin, with chromium mordant, M. H. Koechlin .....                       | 100   |
| „ „ uranium mordant, M. H. Koechlin.....   | 100   |
| Topical style, with artificial alizarin, M. H. Koechlin .....                          | 101   |
| Logwood purple, Messrs. Wood and Wright.....   | 120   |
| Logwood black, Messrs. Heys and Co. ....   | 120   |
| Brazil-wood rose colour, M. H. Koechlin ... ..   | 127   |
| Mock Turkey red, Messrs. Wood and Wright .....   | 132   |
| Schützenberger and Lalande's process for indigo, Messrs, Edmund Potter<br>and Co ..... | 185   |
| Lightfoot's process for chintzes, Messrs. Grafton and Co.....                          | 187   |
| Indigo, dark blue, with light blue reserved, Messrs. Wood and Wright.                  | 201   |
| Same pattern, with discharge printed on, Messrs. Wood and Wright.....                  | 202   |
| Cochineal pink, steam style, Messrs. Wood and Wright.....                              | 217   |
| Ammoniacal Cochineal, Messrs. Heys and Co .....  | 217   |
| Silk dyed with French purple, Messrs. Marnas and Co. ....                              | 232   |
| Eosin, M. H. Koechlin .....  | 252   |
| Quercitron yellow, Messrs. Heys and Co. ....   | 261   |
| Extract of Madder and Quercitron, M. H. Koechlin.....                                  | 262   |
| Fustic, Messrs. Heys and Co. ....  | 268   |
| Persian berries, (yellow), Messrs. Wood and Wright.....                                | 274   |
| Persian berries, (green, with Prussian blue) Messrs. Wood and Wright...                | 275   |
| Lo-kao on silk, Messrs. Marnas and Co.....   | 302   |
| Gallein, M. H. Koechlin .....  | 319   |
| Coerulein, M. H. Koechlin .....  | 320   |
| Catechu brown (light shade), Messrs. Salis Schwabe and Co.....                         | 337   |



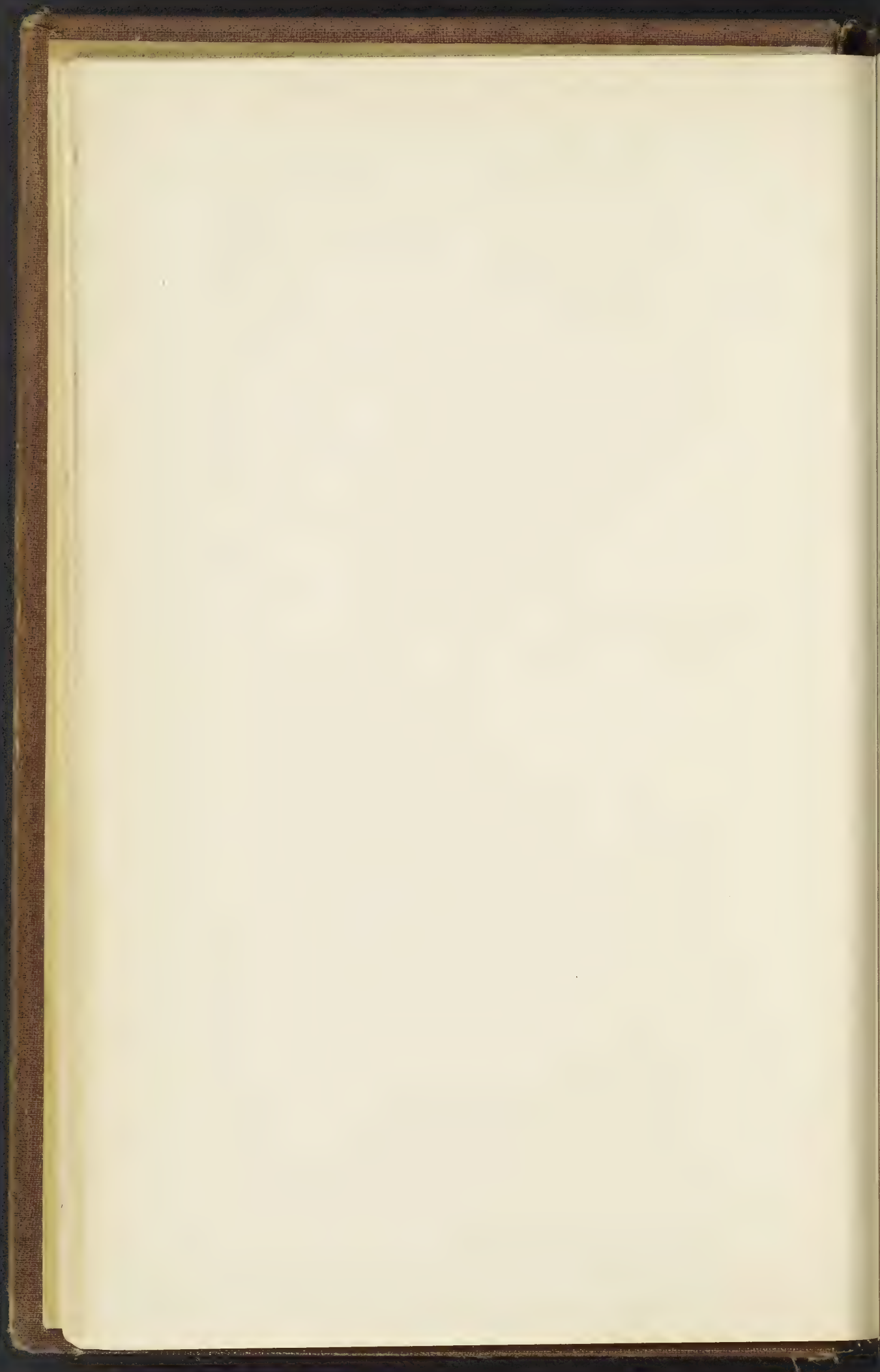
# CONTENTS.

xxix.

|   | PAGE. |
|---|-------|
| Catechu brown (dark shade), Messrs. Salis Schwabe and Co..... | 338   |
| Wool dyed with magenta, M. G. Schaeffer. ....                 | 376   |
| Magenta printed on cotton, M. H. Koechlin.....                | 378   |
| Safranine printed on cotton, M. H. Koechlin. ....             | 381   |
| Hofmann's violet RRR on wool, M. G. Schaeffer.....            | 394   |
| „ „ B on wool, M. G. Schaeffer.....                           | 394   |
| Cotton printed with Hofmann violet, M. H. Koechlin.....       | 401   |
| Wool dyed with aniline blue, M. G. Schaeffer.....             | 408   |
| Nicholson's blue on cotton, M. H. Koechlin.....               | 413   |
| Aldehyde green on cotton, M. H. Koechlin. ....                | 415   |
| Wool dyed with iodine green, M. G. Schaeffer.....             | 420   |
| Methylaniline green printed on cotton, M. H. Koechlin.....    | 423   |
| Aniline yellow on wool, M. G. Schaeffer.....                  | 429   |
| Wool dyed with aniline brown, M. G. Schaeffer.....            | 435   |
| Aniline black on cotton, M. H. Koechlin.....                  | 448   |
| Picric acid on wool, M. G. Schaeffer.....                     | 455   |
| Wool dyed with aurin, M. G. Schaeffer.....                    | 461   |
| Yellow corallin on cotton, M. H. Koechlin.....                | 462   |
| Corallin on wool, M. G. Schaeffer.....                        | 464   |

## LIST OF ENGRAVINGS.

|  |     |
|--|-----|
| Spectra of purpurin and alizarin.....                    | 61  |
| Printing machine.....                                    | 76  |
| Arrangement of bath for dunging.....                     | 78  |
| Arrangement of dyebeck. ....                             | 80  |
| The indigo plant.....                                    | 141 |
| Pastel or Woad.....                                      | 144 |
| Polygonium tinctorium.....                               | 145 |
| Schunck's apparatus for evaporation (cross section)..... | 147 |
| „ „ „ (elevation).....                                   | 148 |
| Apparatus for producing self colours with indigo.....    | 202 |
| Rocella fuciformis.....                                  | 229 |
| Houton-Labillardière's colorometer.....                  | 343 |
| Collardeau's colorometer. ....                           | 344 |
| Wilson's colorometer.....                                | 345 |





DYEING AND CALICO PRINTING.

---

INTRODUCTION.





## CHAPTER I.

### INTRODUCTORY.

NATURE has given to the animal and vegetable kingdoms an infinite variety of colours which from their beauty, their brilliancy, and their purity may vie with the colours of the rainbow, and these phenomena of colour have from time immemorial attracted the attention of enquiring minds and awakened a desire to understand the causes of their production.

The earlier chemists considered that they were due to the presence of a peculiar principle in the cells of organic tissues, which could be acted on by external agents, and that the particular colour produced was determined by the action which took place. Had this view been confined to the colouring principles to be found in the leaves and flowers of plants merely, it would not have been far from the truth, for recent researches have shown that, in the production of all the differences of colour, shade, and tone which we see exhibited in such profusion in the beautiful flowers and foliage of summer, and in the variety and richness of tint in autumn, only two principles are concerned. On the other hand, it was found from a more careful study of the nature of the colours used in dyeing, and a comparison of those colouring matters which had been obtained from certain animal and vegetable substances, and applied to the ornamentation of fabrics, that there were nearly as many

colouring principles as colours, for it was impossible to class the brilliant crimson of the cochineal insect with the yellow extracted from weld, or with the beautiful blue obtained from the indigofera.

When this idea was abandoned, the differences of colour were attributed to a difference in the chemical constitution of the various coloured compounds or colouring principles contained in the cells or tissues, and step by step, by patient observation and persevering study, it has been proved beyond all doubt that there is a considerable number of proximate principles of very different composition and varying widely in properties, but which are classed together under the name of colouring matters or colour-giving principles. It is to the study of these compounds that our attention is at present especially directed.

Before however commencing this study we must consider what is the true cause of colour.

We may define colour as the impression that the light reflected from a surface makes upon the eye.

If a beam of sunlight is admitted into a dark room, through a vertical slit in the shutter, and is then allowed to fall on a vertical glass prism, it will enter it, but on emerging again, will be found to be deflected from its previous path and at the same time decomposed. If the beam of light after its passage through the prism be now received on a white screen, an elongated and brightly coloured image will be seen, which is called the spectrum. This may be roughly mapped out into seven bands of different colours, occurring in the following order:—red, orange, yellow, green, blue, indigo, violet.

Among the bodies found in nature, some absorb the whole of the coloured rays falling upon them, and appear to the eye to be black; others reflect all the rays, and are said to be white; others, again, have the power of decomposing light, absorbing part of the rays and reflecting others.



It is this power of reflecting certain rays which we allude to when we say that anything is coloured. A body is red when it absorbs the other coloured rays, and reflects those which give us the impression of red; it is blue if the blue rays only are reflected, and so on; thus the innumerable shades of colour which we see are caused by the varied combinations of the unabsorbed rays.

It is evident, therefore, that colour is a physical effect produced on the surface of the things that we see, and as the same bodies nearly always appear to us of the same colours, this property of absorbing certain coloured rays and reflecting others must depend on the condition of their surfaces, and on the chemical nature of some of their constituents. In fact we can isolate certain organic principles from coloured organic bodies, which when in a state of purity are remarkable for the variety and intensity of their shades; and these matters, among all the substances of which plants and animals are composed, may therefore reasonably be regarded as possessing the power of acting on light and reflecting certain rays to the exclusion of others. The substances endowed with these properties are what we call the colouring matters or colouring principles of bodies.

On this account Chevreul has defined the art of dyeing to consist in fixing on fabrics by means of molecular attraction, matters which act on light in a different manner from the surface of the fibre itself.

Colouring matters are found in all parts of the animal and vegetable kingdom. We find roots, such as madder, and turmeric; stems of trees, as logwood, and sandal-wood; bark, as quercitron; leaves, flowers, fruits, and seeds as Persian berries, all more or less strongly coloured; again, the liquids circulating in different parts of the body, as the blood, bile, &c., and even whole animals, such as cochineal and kermes, sometimes present very brilliant colours.

The colouring matters are scarcely ever found in the various organisms which enclose them in a pure state, but are mixed with other matters, some of which are derived from or are similar to them, thus rendering their separation a work of great difficulty; on this account comparatively few have been obtained in a state of absolute purity.

It was not until about sixty years ago that any systematic study of the colouring principles of the known dye-stuffs was attempted. Since that time, however, many careful researches have been made, which have included both methods of isolation of the colouring principles, the action of chemical reagents on those principles, and processes for fixing them on fabrics.

Foremost among those who have worked on this subject stands M. Chevreul, who by his careful and successful observation has thrown so much light on the constitution of these bodies, and who perhaps, more than any other man, has rendered the art of dyeing and calico-printing one of the most interesting applications of chemistry to the arts. The researches of Robiquet, Heeren, Kane, Schunck, Gaultiér de Claubry, Persoz, Runge, Kuhlmann, Erdmann, Bolley, Stenhouse, Fremy and Cloëz, Perkin, Martius, Girardin, and many others too numerous to mention, have also rendered valuable service in this field.

Of the colouring matters which have been isolated, some are composed of carbon, oxygen, and hydrogen only, whilst others contain nitrogen also. The fact of their being derived from the animal or vegetable kingdom does not appear to determine the presence or absence of nitrogen, for some of those obtained from vegetables contain nitrogen, whilst some of those obtained from animals are free from nitrogen.

The colours most common in the organic kingdom are reds, blues, and greens, but the latter colour is very alterable and difficult to separate without injury; recourse has



therefore been had to mineral matters of that colour, or a mixture of blue and yellow has been used. Some years ago, however, the green colour from the leaves and stalks of certain plants was imported into Europe, from China, under the title of Lo-kao, and was extensively used. It was afterwards manufactured in France, but is now to a great extent superseded by the coal-tar greens.

Strictly speaking, there are no blacks found in the organic kingdom; browns are formed by the alteration of yellow colouring matters, and are found principally in the barks of trees, the husks of some fruits, and in some milky and resinous secretions which have absorbed oxygen from the air.

Many observations lead to the conclusion that the principles which give to the dyer such beautiful colours are in themselves colourless, and become coloured only on contact with the oxygen of the atmosphere. This may be especially noticed in the freshly gathered leaves of the *Indigofera*, or in the fresh roots of the madder plant, which when growing are both without colour, but soon alter on exposure to the atmosphere, becoming blue and red respectively. The colour-giving lichens are also in themselves colourless, and only yield their colours under the influence of air and alkalis. Brazil and logwoods, when freshly cut, are of a yellowish tint, but both become red on exposure to the air. It is also a matter of common observation that articles of furniture, made of oak, mahogany, or walnut, become darker by age.

The yellow colouring matters of weld, quercitron, and fustic, are, with equal facility, affected by exposure to the atmosphere, soon becoming of a brownish hue. The decoctions of these red and yellow colouring matters are even still more rapidly affected, and if the time of exposure is sufficiently prolonged, crystals of the colouring principles separate, which cannot be obtained from the woods in a living state.

A very striking illustration of the influence of both light and oxygen, in the formation of certain colouring matters from colour-giving principles, was published some years ago by M. Amaudon. He dipped a sheet of blotting paper in an alcoholic solution of guaiacum resin, and dried it quickly in a stove, out of contact with light. He then cut strips from this sheet, and placed them in bottles containing oxygen, one of which was kept in the dark, while the other was exposed to direct sun-light. The latter rapidly acquired a fine blue colour, while the former remained unchanged. On exposing similar strips to sun-light, in bottles containing nitrogen and hydrogen, no change took place. If the paper, coloured blue, be exposed to the more refrangible rays of the spectrum, or a gentle heat be applied, the colour is destroyed by a further oxidation.

On the other hand, when oxygen is removed from many of the colouring matters by means of reducing agents, such as nascent hydrogen, 'sulphuretted hydrogen, the alkaline sulphides, &c., they become colourless, but if again exposed to the air, a reabsorption of oxygen takes place and the colour returns. For example, when an infusion of litmus is shaken in a closed flask, with a little sulphuretted hydrogen, the blue colour in the course of a few minutes passes into a greenish yellow; but, on pouring it out into a shallow vessel, and exposing it to the air, the blue colour rapidly reappears.

From these facts it may be inferred that most of the colouring matters, which have been isolated, are the products of the oxidation or the decomposition of principles in the plants, either colourless or only slightly coloured; these may be considered as *colourable principles*, which by absorption of oxygen become gradually converted into *colouring matters*.

These various principles have in general received names derived from the animals or vegetables which have yielded



them; the more important will be somewhat fully described in the following pages, and others of less commercial importance will be found given in the table at the close of the work.

It is a remarkable fact that the most brilliant and beautiful colours, which are observed in those flowers and parts of the plant most exposed to the sun, are the most delicate and the most difficult to isolate. These organs contain so little of the colouring principle, and it is so fugitive, that when an attempt is made to extract it, it disappears altogether. Generally, in flowers, the colouring principle is fixed in the epidermis or cellular tissue of the petal, for the fluid obtained by expressing the whole leaves is almost entirely colourless.

According to Fremy and Cloëz, all the colours which are observed in flowers, may be referred to three principles only, namely:—cyanin, a compound which is blue or pink; xanthin, a compound of a yellow colour, insoluble in water; and xanthëin, a yellow compound soluble in water.

Cyanin is uncrystallisable, soluble in water and alcohol, but insoluble in ether. Acids, or acid salts, immediately change it to a red and alkalis communicate to it a green colour. It is decolourised by reducing agents, but regains its colour in contact with oxygen. It may be extracted from the petals of the cornflower, the violet, or the iris, by means of boiling alcohol; the flower becomes decolourised, and the liquid assumes a beautiful blue colour. This solution is evaporated to dryness, and the residue treated with water, which leaves undissolved a fatty and a resinous substance. Neutral acetate of lead is then added to the aqueous solution containing the colouring matter, when a beautiful green precipitate falls, which is washed with water and decomposed by sulphuretted hydrogen. The solution of the colouring matter is separated from the sulphide of lead by filtration, and the liquid carefully

evaporated on a water-bath. The residue, after being dissolved in absolute alcohol and precipitated by ether, yields the cyanin in the form of bluish white flakes.

Flowers, like roses, peonies, and some dahlias, when treated in a manner similar to that just described, yield a pink compound. A careful study of the properties of this colouring matter shows that it is identical with, or at least similar to the blue one, and that the pink colour is due to certain juices with which it comes in contact, having an acid reaction, whilst the blue is always found where the juices of the flower are quite neutral.

Xanthin is insoluble in water, alcohol, and ether, and presents the general properties of a resin. It is the mixture of this compound with cyanin in the vegetable juices which gives to flowers the various shades of orange, scarlet, and red. Xanthin may be easily prepared from the sunflower. The flowers are treated with boiling absolute alcohol, which dissolves the colouring matter and deposits it on cooling. It is not pure however, being mixed with a certain quantity of oil, which is removed by a careful saponification and treatment with acid; a mixture of the xanthin and fatty acids is thus thrown down, from which the latter may be dissolved out by cold alcohol, leaving the xanthin in a pure state.

Certain dahlias contain a substance differing from xanthin by being soluble in water. This colouring matter, which has received the name of xanthëin, is soluble in water, alcohol, and ether, but has not been obtained in a crystalline state from any of its solvents. Alkalis communicate to it a rich brown colour, but the original shade is restored by acids. It has great dyeing power, producing on the various fabrics yellow shades of considerable brilliancy. This substance may be prepared from the petals of yellow dahlias, in a manner similar to that followed in the preparation of cyanin from blue flowers,



except that sulphuric acid should be employed for decomposing the lead compound instead of sulphuretted hydrogen; the residue from the aqueous solution is extracted by alcohol, which dissolves the xanthëin, and on evaporation leaves it in a state of purity.

The yellow colouring matters are entirely distinct from cyanin. We know that blue flowers may become red and even white, when the colour is completely destroyed, but they never become yellow; and, on the other hand, yellow flowers never become blue. It is not unusual to see orange flowers become red, but in this case the xanthin is destroyed and the cyanin is left in the red state, modified by the acid juices of the flower.

A great number of flowers open white or pink, and become blue on exposure to the air; others, which are colourless in the bud, become yellow when they are full blown, and as they decay assume a brownish tint. In all flowers the colour is deeper at the outside edge than in the centre.

Although little doubt can exist that the brilliancy and intensity of the colours of flowers is to a great extent dependent on the amount of light they receive, the following interesting experiment of Persoz shows that the roots of plants have a reducing power, and that some colouring matters can be produced by the process of oxidation in the flower. If some stems of balsams, deprived of their roots, be placed in a solution of sulphate of indigo, the solution is absorbed and the stem is soon dyed blue; but if the plant, with the root attached, is placed in the liquor it continues to live and absorbs the solution, but in a colourless state, and the reducing power of the root may be well seen if the solution is exposed to the air, for it will become colourless or slightly green away from the surface, while the part in contact with the air has the appearance of a blue layer. Although in this experiment the stem

remains colourless, the flowers rapidly acquire a blue colour.

M. Becquerel has recently published an interesting series of papers on the action of electricity on flowers. He tried currents of induction, and also sparks from an electrical machine, so weak as to avoid, as far as possible, the production of chemical changes.

On submitting the petals of the *Papaver orientalis*, which have an intense scarlet colour, to the action of sparks from an electrical machine, he found that the part of the petal nearest to the electrical influence was immediately decolourised, and by prolonging the action the entire petal became colourless. On dipping the petal into cold water, the water assumed a violet tint, whilst the petal remained colourless. The petals of the iris, acted on in a similar manner, were entirely decolourised, but yielded their colour to water.

Yellow flowers appeared to undergo little or no change, but if an orange flower, such as a nasturtium, were treated in a similar manner, he found that it yielded to water its red colouring matter, whilst it retained the yellow one.

Heat, or exposure to a cold of several degrees below zero produced the same results, for, when the poppy before-mentioned is dipped for a few seconds into boiling water, the red colour becomes slightly purple; and if it is now placed for some time in cold water, the colouring matter is dissolved and the petals become colourless.

M. Becquerel concludes from these experiments that the walls of the cells of the petals are in all three cases injured, or their organisation so altered that when placed in water it penetrates into the cells, and the soluble red and blue colour is dissolved out, whilst the yellow colouring matter being insoluble and existing in the form of minute granules, is not removed.

The colouring matters possess, as proximate principles and in the free state, a number of characteristics in



common. They are solid, inodorous, and generally tasteless. Many may be obtained in regular crystals, as small brilliant needles; some resemble the resins; others are found as plates and scales, or in globular masses. Their colour in the dry state is often very different from that they have when moist or in solution. Thus carthamin when dry has a coppery appearance, but a magnificent dark red colour when moist; and hæmatoxylin has a pinkish white colour in the dry state; whilst a cold aqueous solution is yellow, and a hot solution orange-red.

All the colouring matters are destroyed at a temperature of 300° to 400° F., giving off products analogous to those obtained in the dry distillation of other proximate principles. Those which contain nitrogen give off ammonia.

But if instead of heating them quickly, they are submitted to a regulated heat, and the temperature is maintained at a point lower than that at which decomposition commences, many of them volatilise; some without any alteration, whilst others give a certain amount of empyreumatic products, which carry over a portion of the substance unaltered, the latter being condensed on the cooler parts of the vessel. By the aid of a current of steam, more or less superheated, they may in many cases be sublimed without any decomposition taking place.

Those colouring matters which can be distilled, either alone or by the aid of steam, are generally faster than the others, being less easily affected by chemical reagents.

Direct sunlight acts on colouring matters in a similar manner to heat, but requires more or less time to produce the change. Scarcely any of the colours will bear a prolonged exposure to strong sunlight, as may be seen in curtains and in those parts of a carpet which are nearest the windows; this effect is also well shown in ladies' dresses, where the inside of the folds retain to a great extent their original brilliancy, whilst the exposed parts are faded.

Some colours, safflower, for instance, are sensibly altered even after a few hours' exposure.

This change is not due to light alone, but requires also the presence of oxygen and moisture, as was shown by Chevreul, who placed the colouring matters of safflower, annatto, and archil under the influence of direct sunlight in vacuo, without producing any change; they may also be kept for a great length of time in the air, provided light be excluded, or even in perfectly dry oxygen and exposed to light, but as above stated they are soon affected by the combined action of light, air, and moisture. The old process of grass bleaching is another familiar illustration of this combined action in removing or destroying colouring matters.

Heat has, to a certain extent, the same action as light. Safflower pink becomes of a dirty white colour in an hour, and the red of Brazil wood undergoes the same change in two hours, when heated to a moderate temperature in a current of moist air. The violet of logwood, the orange of turmeric, and the yellow of weld, all become dark, brown, and tarnished, under the same conditions.

The terms fast and fugitive are used to express the relative action of oxygen on the various colours.

Those bodies which easily give up all or part of their oxygen, on account of their want of stability, are also destructive to colouring matters. Some of them, however, as bichromate of potash, may be used with advantage in fixing certain colours, and this is particularly the case with those obtained from the red woods.

None of the colouring matters can resist chlorine, but its action appears to vary very much according as it is in a moist or a dry state. When dry chlorine is passed over a dry colouring principle, in some instances part of the chlorine is substituted for some of the hydrogen in the compound, whilst another part combines with the hydrogen



so liberated to form hydrochloric acid; but the reaction is always slow, and the substitution is seldom complete. In the presence of water, however, the decolouration is instantaneous, and is probably effected by the nascent oxygen which is liberated from the water by the action of the chlorine.

The hypochlorites also act on colours, but more slowly than free chlorine, and in this case it is the oxygen contained in the compound, and not the chlorine, which is the bleaching agent. Contact with the air (probably on account of the carbonic acid it contains), or the addition of an acid facilitates the action considerably. It is on this account that in bleaching calico the cloth is passed through an acid bath after it comes from the bleaching solution.

Charcoal is also a very powerful decolourising agent, but acts in a manner altogether different from chlorine, as it does not in general alter the colouring matters, but removes them from the liquids holding them in solution. This property it possesses not by a chemical affinity analogous to that which determines their union with metallic oxides, but by a physical or molecular attraction, so that in most cases the unaltered colouring matters may be recovered from the charcoal by suitable methods.

For example, if a weak solution of sulphate of indigo be decolourised by charcoal, the indigo may be removed from the latter by washing it with boiling water, containing in solution a small quantity of carbonate of soda. And by continued washing almost all the indigo may be covered.

The best charcoal for this purpose is that possessing the greatest purity and which is in the finest state of division. Those charcoals which are hard and lustrous, such as anthracite, graphite, or gas coke, are not adapted for removing the colour from liquids; whilst spongy charcoal, light and dull, such as animal charcoal, or that obtained by heating ani-

mal matters with carbonate of potash, and removing the latter by washing with water, possesses the property in a very high degree. The presence of saline or earthy matters in charcoals, as it increases the amount of surface of carbon in contact with the liquid, increases also the decolourising power, and it is on this account that the animal charcoal, obtained by heating bones, is so much more efficacious than that prepared from wood.

Stenhouse found that if an intimate mixture of one part of coal tar and six of quicklime was ignited out of contact with the air, and when cold treated with hydrochloric acid to remove the lime, a charcoal was left which possessed very energetic decolourising powers; also that if vegetable matters be mixed, before calcination, with phosphate of lime, alumina, or clay, a charcoal may be produced which is nearly equal in decolourising power to bone charcoal or ivory-black.

Most of the colouring matters are soluble in water, and always more so in hot water than in cold; their solubility appears to increase with their richness in oxygen. Carotin and indigotin, for example, which contain but very little, are altogether insoluble.

The aqueous solutions alter somewhat rapidly in contact with the air, and lose their colours much more quickly under these circumstances than the moist colouring matters themselves.

Certain saline matters when dissolved in water prevent the solution of colouring matters.

Alcohol, ether, wood-spirit, benzene, chloroform, bisulphide of carbon, glycerin, and the oils and essences generally, dissolve many of the colouring matters freely, and frequently in quantities about inversely proportional to their solubility in water.

Considering the manner in which they act with the preceding reagents, we may view the colouring matters as



divided into two classes, the resinoid and the extractive. To the first will belong those which are insoluble or only slightly soluble in alcohol, ether, and the oils, such as curcumin, carthamin, alizarin, indigotin, &c.; and to the second, those which are soluble in water.

Some of those which are insoluble in water, dissolve in that liquid on the addition of acids or alkalis, thus:— alizarin dissolves freely in concentrated sulphuric acid; santalin and anchusin dissolve in acetic acid; and carthamin, santalin, and bixin dissolve readily in dilute alkalis.

By adding hydrochloric acid, or better still, sulphuric acid, to alcohol or ether, most of the colouring matters may readily be obtained in solution. It was with a mixture of four parts of sulphuric acid, with one of alcohol, that Persoz obtained the greater number of the colouring principles from the dyestuffs which contained them.

Only the more stable colouring matters can be dissolved in acids or alkalis without undergoing alteration; the others undergo a change more or less marked, assuming various shades, which are in some instances characteristic. The colouring matter of flowers already referred to is an example of this, as is also that of the red cabbage.

The changes produced by acids and alkalis on the litmus used by chemists, are due to an action very different from that produced on flowers, for the former really enters into combination with the agents which act upon it. The litmus cakes of commerce are composed of a red colouring matter and an alkali; if this compound is placed in contact with an acid, it is decomposed and the red colouring matter is liberated; on the addition of an alkali the blue compound is again formed.

Concentrated acids and alkalis, at an elevated temperature, entirely decompose all colouring principles, even the most stable. Under the influence of alkalis the colours are modified and destroyed, even if air be excluded; if air be

present, an absorption of oxygen takes place, and a brown colouring matter is formed.

None of the colouring matters can resist the action of nitric acid, but nitrosulphuric acid produces the most rapid and completely destructive action. Ammoniacal cochineal, which is unchanged by sulphuric acid, is immediately decolourised by even a weak solution of nitrosulphuric acid.

The action of sulphurous acid differs from that of the other acids. It has long been used for bleaching silk, wool, straw, &c., and is also used to remove stains made by fruit on colours, which sulphurous acid does not spoil. Some colours, such as cochineal, are not affected by it; some, such as logwood, are completely destroyed, whilst others are simply bleached, and on being exposed to the air, gradually reassume their original tint.

Sulphurous acid acts as a bleaching agent by combining with the colours, and on the combination being destroyed, the original colour is restored. As examples of this:—if a red rose be placed in a vessel containing sulphurous acid, it becomes white in a few minutes; but if it be then dipped in a weak solution of sulphuric acid, it immediately recovers its natural colour, as the latter acid displaces the former. If the bleached rose be placed in chlorine the colour is also restored, for this element converts the sulphurous acid into sulphuric acid. Violets, when placed in an atmosphere of sulphurous acid, are bleached, but on exposing them to ammoniacal vapours they become green, the ammonia not only neutralising the acid, but itself acting on the cyanin and altering its colour.

The anhydrous metallic oxides do not act on colouring matters, but the hydrated oxides combine with them, forming insoluble compounds called lakes. These may be considered as salts, in which the colouring matters play the part of acids, and which can be displaced by stronger acids, as will be seen further on. This affinity of colouring



matters for metallic oxides has been taken advantage of for fixing many colours on fabrics.

The salts, metallic or alkaline, act on the colouring matters sometimes by their acid, sometimes by their base, but more frequently by the latter. In the first case they brighten or change the colour, whilst in the second their oxides combine with the colouring principles, forming insoluble precipitates. If a solution of acetate of lead or chloride of tin be poured into a solution of hæmatoxylin, bresilin, or santalin, precipitates of various colours are produced, which are really lakes or compounds of the colouring matters with the base, whilst the supernatant liquors retain the liberated acid.

In several cases the presence of tissues greatly facilitates this decomposition. In this case the lake is deposited in the tissue and fixed there, so that, to a certain extent, a dyed fabric may be considered as a ternary compound of tissue, metallic oxide, and colouring principle. This is the fundamental principle of the theory of mordants, a name given to salts and other substances by means of which we are able to fix colouring matters which of themselves have no affinity for the fabric. It is, however, rare for a salt to act as a mordant without undergoing decomposition.

Mr. John Thom was the first to observe that there is also an elective affinity of the bases for the various colouring matters, that is, that the bases have a stronger attraction for some colouring matters than for others. An example of this may be seen in alumina, which has a stronger attraction for the principle of madder than for that of logwood, and a greater affinity for the latter than for that of quercitron. When a piece of cloth impregnated with alumina is immersed in a decoction of quercitron bark, it acquires a fast yellow hue; but, if it is afterwards well washed, and then kept for some time in a hot solution of logwood, the alumina parts with the colour of the quercitron to combine

with that of the logwood, and the cloth changes from yellow to purple. If it be now digested for a few hours with a hot infusion of madder, the colouring principle of logwood is turned out, and the alumina unites with that of the madder; the cloth is now found to be red instead of purple. The amount of alumina on the fibre does not appear to be sensibly altered by these substitutions.

Certain salts produce on colouring matters oxidising or even decolourising effects. In the latter instance it is the acids which act, as is the case with the hypochlorites, the chlorates, and the bichromates. In the former case they usually act by their bases; for example, chloride of ammonium mixed with salts of copper forms double salts, which have the property of oxidising the colouring matters and yielding oxide of copper, which, fixing itself along with them in the fibre of the cotton fabrics, gives greater fastness to the colour. The chloride of ammonium cannot in this case be replaced by any other chloride. According to Kœchlin and Plessy this process is especially applicable to the colouring matters of logwood, lima-wood, and catechu.

The salts of gold, silver, and mercury, are reduced by the colouring matters, which combine with the oxygen and are thus altered or destroyed.

The colouring matters combine with the various tissues forming compounds more or less fast. In general they show a greater affinity for animal substances, such as wool and silk, than for vegetable fibres, such as cotton, hemp, and flax, and of these three they have more affinity for cotton than for the other two.

Of the known colouring matters some precipitate immediately upon tissues with which their solutions are in contact, while others cannot adhere to it in a durable manner without the intervention of a second substance which has a more energetic attraction for the colour than the tissue



itself has. To the first class belong indigotin, curcumin, orcëin, and carthamin. Those of the second class are fixed by taking advantage of the affinity which certain metallic oxides possess both for the colouring matter and for the fibre.

The name of 'fast' colours is given to those which resist the action of light, air, water, alcohol, dilute acids and alkalis, and of weak hypochlorites and soap solution. As examples of these may be mentioned the colours derived from madder, indigo, quercitron, cochineal, catechu and gallnuts, and salts of iron.

The term 'loose' colours is applied to those which are quickly destroyed by light and air, and which, notwithstanding their insolubility in water, are removed or altered by dilute acids or alkalis, and by weak hypochlorite or soap solutions. Among these may be mentioned the colours derived from the redwoods, logwood, Persian and Avignon berries, turmeric, annatto, and safflower.

These divisions, however, must be regarded as somewhat arbitrary, and merely useful as a general classification, since we find that in the first class some are much faster than others, whilst in the second some are much more fugitive. Besides this difference, the same colouring principle may give fast colours with some mordants, and loose with others. Even with the same colour and with the same mordant this difference may be observed when the way is varied in which the colour is produced or applied to the fabric. As an illustration of this, we find that when the colouring matter of logwood has been applied to a tissue by means of a salt of alumina, the purple thus obtained is not washed away by water, but is rapidly altered by exposure to the atmosphere; when, on the contrary, it has been applied as a pigment, by means of a salt of tin, although it resists the action of the atmosphere, it is almost entirely removed by boiling water; whilst, if it be treated with bichromate of

potash, it becomes fit to resist both water and atmospheric influences. Again, if one piece of mordanted cloth is dyed in a bath containing Alsatian madder and water only, whilst a second piece is dyed in a bath of the same madder containing also a little chalk, or in one of Avignon madder, we find such differences as would lead us to imagine that they are altogether different dyestuffs; or, by placing together a steam-pink and a pigment pink, it appears impossible to believe that they contain the same colouring principle, the steam-pink resisting every agent that does not act on madder reds, whilst the pigment pink is much more easily altered by exposure to the atmosphere and is readily discoloured by soap.

Chevreul, by a series of interesting experiments, proved that colours vary considerably in their power of resisting heat in vacuo, and that some, which are very fugitive under the influence of air and light, or of soap, remain fast, whilst others resisting these agents are much injured by heat.

Turmeric, which fades so rapidly in the air, may be exposed on cotton and silk to a temperature of  $320^{\circ}$  F. in vacuo, without any alteration. Brazil wood, cochineal, quercitron, weld, and orchil, fixed by alum and tartar on cotton or silk, undergo little or no change under similar circumstances. Logwood, fixed by the same process, undergoes a remarkable modification, the blue purple becoming a red purple, as if it had been treated with an acid. Logwood, Brazil wood, and cochineal, fixed by a tin mordant, have a greater tendency to alter than when fixed by an alumina mordant.

The nature of the fabric also may have an influence on the fastness of a colour under these circumstances, as it has also when exposed to light. For instance, safflower may be exposed to  $320^{\circ}$  F. in a vacuum, without injury when dyed on silk, but on wool or cotton it is much altered. Annatto similarly treated is less fast on silk than on cotton.



The influence of the fabric is shown also by the joint action of air and heat. Indigo, thus treated, is more fixed on silk than on cotton. Sulphindigotic acid at  $320^{\circ}$  F. is only slightly altered on silk and cotton, but much more so on wool, and steam has a tendency to turn it green, especially on wool and silk; and on wool dyed in the vat, the colour is weakened at  $320^{\circ}$  to  $350^{\circ}$  F., and assumes a greenish hue.

Indigotin, sulphate of indigo, and also Prussian blue, although stable on cotton, are not so on wool; and, for the same reason, namely, a certain reducing action of the fabric.

All Chevreul's experiments on these interesting points, show that cotton exerts very little reducing power on colouring matters, whilst silk, and especially wool, possess it to a considerable extent.

It may be mentioned also, in passing, that this chemist proved that even so fast a colour as Prussian blue could be entirely decomposed by light, for he found that a piece of woollen dyed with Prussian blue when placed in a vacuum and exposed to the direct rays of the sun, lost all its blue colour, and became of a slightly yellowish tint. On exposure to the air in a dark place it resumed its original colour.

## CHAPTER II.

### MADDER.

This well-known tinctorial substance may still be considered as the most important of all the dyestuffs employed by calico printers, owing to the brilliancy and variety of shade and colour that can be obtained from it; one dyeing operation being sufficient to produce pinks, reds, purples, violets, puce, and black. Besides this they are permanent under the action of light and soap, and the wear and tear to which they are exposed during the processes of dyeing and clearing.

The employment of madder-root as a dye dates from the most ancient times, as some of the fabrics used by the Egyptians for enveloping their mummies are dyed with it. The Greeks and Romans were also acquainted with madder under the names of *Erythrodanon* and *Rubia*, and their modes of fixing it on cotton fabrics were the same as those now employed, namely, aluminous salts for producing reds, and salts of iron for purples and blacks. Although it is probable that it has been cultivated in Italy ever since that time, yet it was only introduced into Holland in the sixteenth century and into Alsace in the seventeenth. It is curious to remark that its introduction into Avignon in 1762 was due to an Armenian who brought the plant with him from the East.

The plant which produces madder is an herbaceous perennial called *Rubia tinctorum*. It bears a yellow flower,



and its fruit is a dark red berry. The red colouring matter exists almost entirely in the cortical part of the root, little or none being found either in the epidermis or in the ligneous or centre part of the root. Decaisne and Schwartz have stated that there is only one colouring matter in the root, that it is yellow, and that it becomes red under the oxidising influence of the atmosphere. These results have since been confirmed by Grelley, Gerber, and Dolfus. (The researches of Schunck, which will be referred to further on, show that the colouring matter does not exist in the plant in a free state, but in combination with a sugar; to this glucoside he gave the name of rubian.)

The oxidising process goes on to a certain extent, in the roots of the plant when they are allowed to remain for several years in the ground, especially in chalk formations. In France the roots are allowed to remain in the ground two or three years; in Turkey and the East, from five to seven. In the latter countries and in Naples they are dried in the open air, but in Holland and France stoves are employed for this purpose. Naples and Turkey madders are imported in the root, and are known in commerce as Naples and Turkey roots, whilst those from France and Holland are ground and sold under the name of French and Dutch madder.

The importance of this trade on the continent may be judged of from the fact that in one of the departments of France, Vaucluse, there are about fifty mills turned by water power, which grind eighty millions of lbs. per annum. The quantity grown in this department alone represents a value of about a million sterling.

One hundred parts of fresh root, yield on perfect desiccation, twenty parts of the dried substance, and the roots, as imported, always contain from 16 to 18 per cent. of water; the fresh roots, therefore give about 24 or 25 per cent. of commercial madder. Dutch and Alsatian madder, after

being ground, is stored in large casks and kept for two or three years, when the colouring matter is developed, and its tinctorial power much increased; if kept five or six years, however, further changes ensue, and its value seriously decreases. French Avignon madder, on the contrary, can be employed at once, although the quality is much improved by keeping it for one or two years. The best Avignon madders are grown on lime formations. The roots which have a red colour are called "palus," and those that are pink "rosées;" the former being considered the finer. The values of these madders are in proportion to the fineness of their powders, the finest powder containing the most colouring matter. One hundred parts of dried madder root consist of—

|  |           |
|--|-----------|
| Matter soluble in cold water .....   | 55 parts. |
| „ soluble in boiling water, and containing the greater part of the colouring-giving principles ..... | 3 „       |
| „ soluble in Alcohol .....   | 1.5 „     |
| Fibrous matter.....  | 40.5 „    |

The nature of the chemical changes, which occur in madder during the time it is stored, and which so much improve its commercial value, was entirely unknown until the year 1851, when the elaborate and interesting researches of Dr. E. Schunck were published. This chemist succeeded in isolating a peculiar ferment called *erythrozym*, which possesses the property of decomposing a substance existing in the root, and called by him *rubian*. Rubian may be considered as a glucoside (the name given to compounds of sugar with other organic principles), which is decomposed by the erythrozym into alizarin and a peculiar sugar.

The following is a slight sketch of our present knowledge of the colouring matters which have been obtained from the madder root. Robiquet and Collin, in 1824, were the first to isolate any distinct chemical compound from madder; this they did by heating it with strong sulphuric



acid, whereby it was converted into a black mass, the so-called *charbon-de-garance*, which on being carefully heated, yielded a sublimate of beautiful orange-coloured crystals. To this substance they gave the name of *alizarin*, and in 1828 the same chemists isolated purpurin, another colour-giving principle. About the same time Kuhlmann extracted a bitter yellow compound which he called *xanthin*.

Although between this date and 1851 many chemists attempted to discover the nature of the colouring principles in madder, no accurate information was attained until the publication of Schunck's series of elaborate papers, which threw quite a new light on the subject.

The experiment by which he proved that there is no free colouring matter in fresh madder roots, and that its production is entirely due to the action of a ferment, is as follows :—

Some madder roots having been taken out of the ground, and cut small without being dried, were found to produce colours when used for dyeing in the ordinary manner. But on treating the roots, after being cut into pieces as quickly as possible, with boiling alcohol, a yellow extract was obtained, which contained rubian, but which, even after all the alcohol had been driven away, was found incapable of imparting to mordants any but the faintest shades of colour; whilst the portion of the root left undissolved by alcohol, on being subjected to the same test, imparted to the cloth no more colour than the extract. It was evident therefore that the alcohol had effected a separation between the colour-producing body and the agent, which, under ordinary circumstances, is destined to effect its transformation into colouring matter.

To this special ferment, which is insoluble in alcohol, he gave the name of *erythrozym*. The value of the discovery that colouring matters existed in plants in the state of glucosides, and that they were unfolded by special fer-

ments, cannot be too highly estimated; an idea of its importance may be formed from the fact that it has enabled Schunck to explain the production of indigo from the plant which yields it; that it has lead to the isolation of several other colouring principles; and that it throws much light on the chemical changes which take place in madder roots from the time they are gathered to the time they are used. There is no doubt that the changes taking place while the madder is stored (the time varying as before stated from two to six years according to the country in which the madder is grown) are due to the action of the erythrozym, which gradually resolves the rubian into sugar and alizarin. Whether there are various other glucosides which are decomposed by the ferment giving rise to purpurin and the other colouring matters, or whether all these are formed by gradual oxidation from one colourless substance which is liberated by the action of the ferment, is a point not yet satisfactorily explained. The researches of Emile Kopp, Schützenberger, and Bolley support the latter view, whilst Schunck appears to be in favour of the former.

To prepare erythrozym, Schunck places a quantity of madder in a piece of calico, and for every pound of the root pours upon it four quarts of distilled water at 100° F. To the extract so obtained, an equal volume of alcohol is immediately added, which causes the precipitation of dark reddish-brown flocks; these after being collected on a filter and washed with alcohol until the filtrate is colourless, leave a mass which has the same feel as casein; when dried it coheres into hard lumps which are almost black.

Erythrozym becomes insoluble in water after it has been once precipitated by alcohol, and it is an interesting fact that its power of producing fermentation appears to be restricted to rubian, for the glucosides from other plants, such for example as those of indigo, do not undergo any change when submitted to its action.



Erythrozym possesses in an eminent degree the power of effecting the decomposition of rubian. If a mixture of the two substances be left to stand at ordinary temperatures, a complete change takes place in the course of a few hours. The liquid is converted into a jelly of a light-brown colour, perfectly tasteless, and insoluble in cold water.

The aqueous solution of erythrozym is coagulated when heated to its boiling point. This important fact ought to warn madder dyers to avoid carrying their dyebecks too rapidly to the boil; and it appears highly probable that if they were to moisten the madder with tepid water, and leave it to stand for several hours, or even days at a moderate temperature, previous to its being employed in the dyebecks, they would materially increase its dyeing powers. Certain salts, among which may be mentioned common salt, also coagulate this ferment.

Schunck found erythrozym to be a compound of lime with a nitrogenous substance, and that if the lime were removed by means of an acid, the erythrozym lost its power of inducing fermentation, which moreover was not restored on the addition of fresh lime to replace that which had been removed. This observation would naturally suggest that a little chalk ought to be added to the dyebeck, in using madders or roots which have been either badly stored or stored too long, and in which an alcoholic, acetic, or lactic fermentation had taken place and so made them acid; it also explains why it is found so advantageous to add chalk to the dyebeck when using certain classes of madder, such as Turkey roots, or Dutch or Alsace madder, for the chalk prevents the removal of the lime from the ferment which would then be rendered inert.

According to Schunck, the elementary composition of erythrozym is  $C_{56}H_{34}N_2O_{40} + 4CaO$ .

It will now be advisable to give a short account of the properties and characteristics of the most important prin-

ciple discovered by Schunck, viz., *rubian*, and then to describe the action of erythrozym upon it.

To obtain rubian, Avignon madder is placed on a piece of calico stretched on a wooden frame, and boiling water poured over it in the proportion of four quarts to each pound of madder. To the yellowish-brown liquor thus obtained, whilst still hot, animal charcoal is added in the proportion of one ounce for every pound of dyestuff. The whole is then well stirred and allowed to settle. The charcoal after being collected on a filter is washed with cold water until all the chloregenin is removed, which is the case when the percolating liquid on being mixed with hydrochloric acid and boiled, no longer acquires a green colour. The charcoal is then boiled with successive quantities of alcohol as long as the liquid continues to acquire a yellow tint, and the solution is evaporated. To get rubian quite free from chlorogenin, Schunck advises the use of charcoal which has previously been used two or three times for a similar operation. The sulphides of lead and tin possess the same property at the time of their formation, but the charcoal process is the most convenient and economical.

Rubian is a hard, brittle, and shining substance, similar in appearance to gum. It is soluble in water and still more so in alcohol, but insoluble in ether, which precipitates it from its alcoholic solution. Its solutions have an intensely bitter taste. It gives no precipitates either with mineral or organic acids, with alkalies, or with salts of alumina or iron, &c.

The above facts threw quite a new light on the substance *xanthin*, discovered, as already stated, by Kuhlmann. He obtained it by acting on madder with boiling alcohol, evaporating the extract to dryness, and treating the residue with water. It was further purified by converting it into a lead compound and subsequently decomposing it with dilute sulphuric acid. The substance was thus ob-

tained as a viscid mass of a bright orange hue, soluble in water, and having a bitter taste. It was proved by Schunck to be a mixture of rubian and chlorogenin, for by treating an aqueous solution of xanthin with animal charcoal, he succeeded in separating the rubian from the chlorogenin. It was formerly supposed by chemists that the injurious action of xanthin was due to its becoming oxidised under the influence of the heat of the dyebeck and the oxygen of the air into a brown substance, which, fixing itself on the cloth, soiled the whites and spoiled the colour; now, however, it is evident that this is caused solely by the chlorogenin which it contained. Rochleder has given this latter compound the name of *rubichloric acid*.

In October, 1848, Mr. Higgin, of Manchester, published a paper in the Philosophical Magazine, in which he stated that xanthin could be recognised by its yellow colour, and the bitter taste of its aqueous solution, which he considered as characteristics; and that when the extract of madder was left at a temperature of 130° F. this compound gradually disappeared, and a gelatinous or flocculent substance was produced, which possessed all the tinctorial power belonging to an infusion of madder. He concluded from this that the xanthin was converted into alizarin during the process. Schunck states that these researches gave him the clue to unravel this intricate subject, so that he was ultimately enabled to offer an explanation of the phenomena which take place during the fermentation of madder.

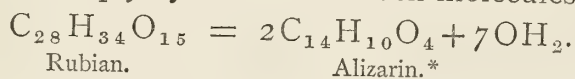
The following, taken almost verbatim from a paper read by Dr. Schunck before the Chemical Society, in the year 1860, gives a clear resumé of his researches on the actions of erythrozym, acids, and alkalis on rubian and also of the products of its decomposition.

At first sight the change which rubian undergoes, when



decomposed by means either of acids, alkalis, or ferments, would seem to be simple enough. It might be supposed to consist in a splitting up of its complex molecule into alizarin and sugar, and to resemble many analogous processes with which we are acquainted; the result being the formation of sugar and another body, the two together having originally formed a conjugate compound; this, however, is not the case, for the products of decomposition never consist of alizarin and sugar alone. The part insoluble in cold water contains in all cases, besides *alizarin*, two resinous bodies, one, *rubiretin*, easily soluble in alcohol; the other, *verantin*, less soluble in that liquid. These bodies, although resembling resins in some respects, must be classed as colouring matters, since their colour seems to be inherent and not a merely accidental property. But in addition to these, there is uniformly found accompanying the alizarin, a third body belonging, as far as general appearance and properties are concerned, to the same class of substances as rubiacin. This third body is, however, in each case quite distinct. When acids have been employed for the decomposition of rubian, this third body, which is called *rubianin*, is found to have the following properties:—It is tolerably soluble in boiling water, and crystallises in lemon-yellow silky needles; it is decomposed on being heated, but resists the action of nitric and concentrated sulphuric acids. When alkalies are used instead of acids, rubianin is replaced by *rubiadin*, which is a body crystallising in beautiful golden-yellow scales, insoluble in water but soluble in alcohol, and is completely volatilised when heated. But when rubian is decomposed by fermentation, it yields neither of these two, but in their place *rubiafin*, a substance resembling rubiadin in most of its properties, but easily distinguished from it by passing into *rubiacic acid* when treated with perchloride of iron. This substance is usually accompanied by another of similar

properties of which it is difficult to say whether it must be considered as distinct from the others, since it has not been obtained in a state of purity,—it is called *rubiagin*. Now all these bodies which accompany alizarin make their appearance so invariably on the occasions named, that their appearance cannot be considered accidental. Let us see, therefore, how their simultaneous formation from rubian is to be explained. The formula assumed for rubian is  $C_{28}H_{34}O_{15}$ . Hence it follows that rubian is converted into alizarin simply by the loss of seven molecules of water.



The formation of verantin and rubiretin, is due to another kind of decomposition. The formula of these two bodies being  $C_{14}H_{10}O_5$  and  $C_{14}H_{12}O_4$  respectively, it will be seen that by adding the two together, we obtain one equivalent of rubian minus six molecules of water. The composition of the class of bodies to which rubianin belongs is rather doubtful. It is probable that the formula of rubianin is  $C_{22}H_{24}O_9$ . If so, it is formed from rubian by the separation from the latter of one equivalent of grape-sugar. Rubiafin, however, being easily convertible into rubiacic acid, must contain sixteen equivalents of carbon, and its formula is therefore probably  $C_{32}H_{26}O_9$ , that of rubiadin being the same.

It appears from this that rubian undergoes not one, but three different processes of decomposition, when acted on by acids, alkalies, or ferments; that the formation of sugar is connected, not with that of alizarin but with that of rubianin and its allies, and that in fact there is no reason

---

\* Schunck believed the formula of alizarin to be  $C_{14}H_{10}O_4$ ; it has since been proved, however, that it is  $C_{14}H_8O_4$ , so that either the decomposition takes place in a manner different to that represented, or the formula assigned to rubian is incorrect; the latter supposition is very probable, as it is amorphous and consequently its physical properties are no guarantee for its purity. The same remark applies to the other non-crystalline products obtained from madder.—EDS.



why one of these processes should not take place to the exclusion of the others; for instance, rubian might be so decomposed as to yield alizarin alone without any of the accompanying bodies, which, in practice, are not only a source of loss, but are actually prejudicial.

Although in the foregoing quotation Dr. Schunck considers that rubian is decomposed by erythrozym into alizarin and water, simply; yet more recent researches have induced him to believe that in part at least there is a decomposition into alizarin and sugar.

When a solution of rubian is boiled with a considerable quantity of sulphuric acid for some time, and is then allowed to cool, it deposits a large quantity of orange flocks, which, when washed with water until all traces of acid are removed, are found to consist of four different substances, alizarin, verantin, rubiretin, and rubianin.

Alizarin is easily separated from the other substances: the flocks are dissolved in alcohol, and hydrate of alumina added, which combines with the alizarin. The lake is thrown on a filter and washed, and then treated with carbonate of potash or soda until all the alizarin is dissolved. On the addition of an acid to the solution the alizarin is thrown down and is collected on a filter. It is then dissolved in alcohol, from which it crystallises as dark yellow crystals without any tinge of brown or red. It differs from the alizarin obtained by sublimation, which will be described further on, by containing three molecules of water.

*Verantin.*—On treating the above-mentioned alcoholic solution of the orange flocks with a solution of neutral acetate of copper, verantin is precipitated together with oxide of copper, from which the oxide may be removed by acids.

The verantin so obtained is a reddish-brown powder of a resinous nature which when heated in a test tube gives a



small quantity of an oily substance without any trace of crystals. It does not communicate any colour to mordanted cloth, and therefore cannot be considered as one of the colour-giving principles of madder.

*Rubiretin* was obtained by Schunck as a brown, opaque, resinous mass, brittle when cold, but becoming soft and almost melting in boiling water. It communicates to alcohol a dark yellow colour, and dissolves in alkalis, forming a brownish-red solution, from which it is precipitated on the addition of an acid. It has no dyeing powers.

The two last-named substances were found by Schunck to exist in garancin, and in his opinion they are removed or modified under the influence of high-pressure steam during the transformation of garancin into 'commercial alizarin.'

*Rubianin*.—When acids have been employed to decompose rubian, a fourth body, rubianin, is obtained; when alkalis have been used the substance produced is *rubiadin*, and when fermentation by erythrozym has taken place it is *rubiafin*. All these bodies are soluble in water, from which they crystallise in well-defined yellow needles.

In 1847, Dr. Schunck obtained directly from madder two interesting substances, which he named *rubiacin* and *rubiatic acid*, the former being identical with the madder orange discovered by Runge.

The best method of preparing rubiatic acid is as follows. The waste liquor from the dyebeck is strained through a cloth, and hydrochloric acid added. A brown flocculent precipitate is thrown down, which is collected on a calico filter and treated with pernitrate of iron until nothing more is dissolved. After filtration hydrochloric acid is added, which throws down a yellow precipitate. This precipitate is dissolved in boiling carbonate of potash, and on cooling yields crystals of rubiate of potash. On the addition of

a strong acid to the solution, the rubiacic acid is precipitated as a bright lemon-yellow coloured powder. Its formula is  $C_{16}H_8O_8$ . It cannot be obtained in a crystalline form. It is only slightly soluble in boiling alcohol, is soluble without decomposition in cold strong sulphuric acid, but is decomposed by strong nitric acid. Its characteristic property is its solubility in perchloride of iron, with a reddish-brown colouration. It is precipitated in yellow flocks from this solution by the addition of an acid. The potassium salt forms beautiful well-defined crystals of a light brick-red colour.

If a current of sulphuretted hydrogen be passed through a solution of rubiacic acid, oxygen is removed, and the acid is converted into rubiacin, to which Schunck has assigned the formula  $C_{16}H_{10}O_5$ . On adding chloride of barium to the sulphuretted hydrogen liquor, a dark purple precipitate is produced, which after being thoroughly washed with water and treated with hydrochloric acid yields rubiacin. By crystallization from boiling alcohol this substance may be obtained in beautiful yellow crystalline needles and plates, having a high lustre.

It is only slightly soluble in water but very soluble in alcohol, and also in acetic and sulphuric acids, from which it is reprecipitated without change on the addition of water. It is very interesting to observe that rubiacin absorbs oxygen from persalts of iron, being converted into rubiacic acid, whilst it is not so completely oxidised by nitric acid.

Like all this class of substances it yields a blood-red solution with potassium carbonate, and a dark brown-red with feric salts. With caustic alkalis it gives a reddish purple solution, from which it is precipitated by acids. It only produces a dirty brown colour on mordanted cloth.

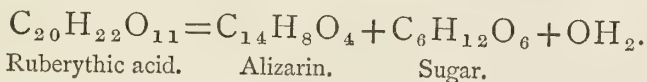
Schunck states that none of these substances, except alizarin, contribute to the production of fast colours during the process of madder dyeing; and, moreover, that they are

very injurious to the strength and beauty of the colours produced from the alizarin.

*Sugar.*—This was obtained from rubian by completely decomposing it with dilute acid. It is a yellow syrup, having no tendency to crystallise.\* Heated at 212° F. it loses a portion of its water, and becomes brittle and capable of pulverization. By the action of nitric acid it is slowly converted into oxalic acid. It is not precipitated from its aqueous solution by any metallic salt, not even by subacetate of lead. Like grape sugar it becomes brown when boiled with an alkali, and yields alcohol and carbonic acid by fermentation with yeast. It has the same composition as grape sugar.

For the purpose of convenient reference, a very complete and elaborate table, drawn up by Dr. Schunck, is inserted at the end of the book, in which he gives the principal colouring matters studied by him, with their formulæ and properties.†

Rochleder, several years ago,‡ published some interesting researches, in which he states that he succeeded in obtaining a crystallised glucoside of alizarin, to which he gave the name of *ruberythric acid*.  $C_{20}H_{22}O_{11}$ . When quite pure it crystallises in silky prisms, only slightly soluble in cold water, but very soluble in hot. It is soluble also in alcohol and ether, and on being boiled with dilute mineral acids it is converted into alizarin and sugar.



Ruberythric acid.      Alizarin.      Sugar.

Although admitting that Rochleder has obtained this

\* Cane sugar appears to exist in madder as such: on one occasion a deposition of hard crystals of sugar was observed in an alcoholic extract of madder which had been kept for some time.—C.E.G.

† For complete details the reader is referred to Schunck's report to the British Association for the Advancement of Science, 1847 and 1848, and to the Philosophical Transactions of the Royal Society, 1851, 1852, 1853.

‡ Jour. für Prakt. Chem. lv. 385 and lvi. 85.



glucoside of alizarin, Schunck maintains\* that it does not exist as such either in madder or in rubian, but is a product of the oxidation of rubian under the influence of alkalis. He prefers to give it the name of *rubianic acid*.

Rochleder has recently found† that, besides alizarin and purpurin, garancin contains small quantities of four yellow crystalline substances. The one which is the most abundant, and which he calls *isalizarin*, has the same composition as alizarin,  $C_{14}H_8O_4$ . It differs from that compound, however, by the red colour of its alkaline solutions, which is intermediate between that of alizarin and that of purpurin, and it gives no colour on mordanted cloth. The second substance, *hydralizarin*,  $C_{28}H_{18}O_8$ , has a paler hue than isalizarin, and communicates to a hot solution of perchloride of iron a brown colour, from which, on cooling, it separates in the form of yellow flocks. The other two bodies, which occur in very small quantity, have the formula  $C_{15}H_{10}O_4$  and  $C_{29}H_{20}O_8$ , but no name has at present been assigned to them.

According to Schützenberger, madder contains rubian, ruberythric acid, alizarin, purpurin, an orange substance pseudopurpurin, and purpuroxanthin.

The two first-mentioned have been already described, and alizarin and purpurin are so important that they will be noticed at length further on. The three other colouring matters, discovered by Schützenberger in 1867,‡ he obtained from Kopp's so-called commercial purpurin by treating it with benzene and alcohol.

He states that *pseudopurpurin* is nearly insoluble in alcohol, but very soluble in boiling benzene, from which it crystallises on cooling under the form of fine needles of a brick-red colour. It is converted into purpurin by the

---

\* Jour. Chem. Soc., 1860, p. 216.

† Deut. Chem. Ger., Ber. iii. 292.

‡ Schützenberger. Traité de Matières Colorantes.

action of heat, and the same transformation takes place when it is dissolved in alcohol and heated under pressure at a temperature of 400° F.

The orange substance is insoluble in boiling benzene, but very soluble in hot alcohol, from which it separates in orange scales. It is soluble in boiling water. When heated it splits up into purpurin and water, and is therefore regarded as a very stable bi-hydrate of purpurin.

The yellow colouring matter, *purpuroxanthin*, is soluble in alcohol and benzene, but only slightly soluble in water. It may be sublimed without decomposition. The faint yellow colour which it imparts to alumina mordants is easily removed either by soap, or by nitro-muriate of tin.

This compound may also be obtained from purpurin, pseudopurpurin, or the orange-coloured hydrate above mentioned, by the action of reducing agents, such as hydriodic acid, or by dissolving them in soda, adding protochloride of tin until the solution acquires an orange colour, and then precipitating with hydrochloric acid.

These compounds, which Schützenberger states exist naturally in madder, appear to be the products of the successive oxidation, either of a colourless unknown principle or of alizarin, which when liberated from its combination with sugar, might form the various compounds described.

Schützenberger describes as follows the colours and tints which each of the substances above mentioned yield to mordanted cloth when dyed with proper precautions :—

Alizarin gives the usual colours which resist the action of soap and nitro-muriate of tin. The reds are of a violet tint, and the violets extremely pure.

Purpurin and the orange compound resist fairly the action of soap and nitro-muriate of tin. The reds are very bright; the violets dull and greyish.

Pseudopurpurin dyes up the mordants, but the colours so

produced do not resist the action either of soap or of nitro-muriate of tin. The reds are clear, having a slight orange hue; violets weak.

Purpuroxanthin gives colours which do not resist either soap or nitro-muriate of tin. With an alumina mordant it gives orange-yellow shades, and with iron pale grey.

Of the three colouring principles, isolated and described by Schützenberger, only one, the orange compound, can be considered as a true colour-giving principle; the other two, pseudopurpurin and purpuroxanthin, possess no commercial value, as they do not yield fast colours.

He makes the interesting remark that the fastness of the colour-giving principles of madder is in inverse ratio to the proportion of oxygen which they contain.

Rosenstiehl\* has recently examined the colouring matters existing in madder which he states to be four in number, alizarin, pseudopurpurin, purpurin, and purpurin hydrate. When pseudopurpurin,  $C_{14}H_8O_6$ , is boiled with water, it is transformed chiefly into purpurin,  $C_{14}H_8O_5$ , and hydrate of purpurin, but a small quantity of purpuroxanthin,  $C_{14}H_8O_4$ , is simultaneously produced. This reducing action takes place more readily in acidulated water or in a solution of alum.

M. Martin, of Avignon, states that all these compounds may be easily converted into alizarin by means of reducing agents in the following way :—

They are dissolved in concentrated sulphuric acid, and when solution is complete zinc powder is added; heat facilitates the action, and renders it more certain. When it is finished, the mass is thrown into water, and an abundant precipitate of alizarin is obtained, which it is only necessary to wash to have in a state for printing.

*Alizarin.*—It was, as already stated, discovered in 1828, by Robiquet and Colin. But a more convenient process for

---

\* Compt. Rend. lxxix., 680.



obtaining it, in the anhydrous state, was devised by Schwartz, in 1856. The alcoholic extract, obtained from garancin, dried and reduced to fine powder, is laid upon a sheet of filtering paper, which is placed on an iron shovel, so as to enable the operator to apply heat cautiously in order that the paper may not be charred. The extract soon melts, the paper absorbs a brown resinous matter, whilst the alizarin sublimes on the surface of the mass in the form of beautiful orange-coloured crystals. Pure alizarin melts at  $527^{\circ}$  F., and sublimes at a high temperature. It has a dyeing power ninety-five times as great as that of madder.

It may be stated, as a fact very interesting, although of no commercial value, that if superheated steam be passed over the preparation of madder known as garancin, pure alizarin is volatilised, and may be easily collected. The best source of alizarin, however, is Kopp's green alizarin, from which it may be extracted by hot petroleum, in the manner which will be described when treating of Kopp's process for extracting the colouring matters from madder.

When alizarin, obtained by Schwartz' process, is dissolved in ether, and the ether allowed to evaporate slowly, it is obtained in the form of beautiful golden-coloured scales, containing two equivalents of water. It exists, therefore, in three forms:—

|                            |                         |
|----------------------------|-------------------------|
| Anhydrous .....            | $C_{14}H_8O_4$ .        |
| Bihydrate (Schwartz) ..... | $C_{14}H_8O_4, 2OH_2$ . |
| Trihydrate (Schunck).....  | $C_{14}H_8O_4, 3OH_2$ . |

Different formulæ have been assigned to alizarin ; the two which were formerly most generally adopted being those of Schunck,  $C_{14}H_{10}O_4$ , and Strecker and Wolff,  $C_{20}H_{12}O_6$  ; but the recent discovery of artificial alizarin, by Graebe and Liebermann, and the examination of its products of transformation have completely established the formula which they proposed, viz.,  $C_{14}H_8O_4$ .

Cold water dissolves a mere trace of alizarin; it begins to dissolve more readily at 160° F., and the solvent power of the water increases as the temperature is raised, as may be seen by the following table:—

|                                 |               |
|---------------------------------|---------------|
| At 212° F. water dissolves..... | 034 per cent. |
| 300° F. „ .....                 | 035 „         |
| 400° F. „ .....                 | 820 „         |
| 440° F. „ .....                 | 1700 „        |
| 480° F. „ .....                 | 3160 „        |

Schützenberger, in pursuing these experiments, succeeded in obtaining alizarin and purpurin, in a crystalline form, from an aqueous solution under very high pressure, or better from a mixture of nine parts of water with one of alcohol at a temperature of 480°-530° F.

Alizarin is freely soluble in alcohol, ether, wood-spirit, benzene, turpentine, carbon bisulphide, and glycerin. It is soluble without decomposition in sulphuric acid, and is not decomposed by it even at a temperature of 400° F., being thrown down unchanged when the acid is diluted with a large quantity of water. It is soluble in a hot solution of alum, but insoluble in a cold one.

Schützenberger was the first chemist who succeeded in reducing alizarin, which he effected by heating it to a temperature of 350° F. with hydriodic acid and phosphorous in sealed tubes. A more simple process is that of Bolley and Rosé, which consists in heating in a closed vessel a solution of alizarin in potash with zinc and iron. The alizarin gradually loses its purple colour, and assumes a yellow tint; hydrochloric acid is then added, and the precipitate produced is washed with boiling water. These operations must be conducted with great care, so as to prevent the alizarin becoming reoxidised by exposure to the atmosphere. The compound thus formed may be regarded as a hydride of alizarin. It is decomposed by heat.\*

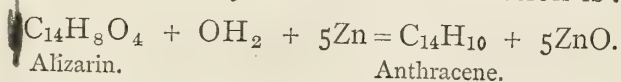
---

\* *Moniteur Scientifique*, 1866, vol. viii, 981.

If aldehyde be added to an alkaline solution of alizarin, the purple liquid becomes orange on the addition of an acid; yellow flocks being precipitated.

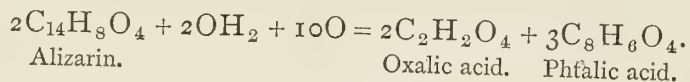
Graebe and Liebermann, in 1868, found that when alizarin is distilled with powdered zinc, it is converted into anthracene, and it was this fact which lead them to employ anthracene in their attempts to produce artificial alizarin.

The equation given by them for this reaction is :



Berthelot found that by heating alizarin with hydriodic acid in sealed tubes, hydrocarbons were formed varying according to the proportions employed; with excess of the reducing agent hexane and octane are the principal products.

Alizarin is easily oxidised by nitric acid, and is converted into oxalic and phtalic acids, as shown by the equation :



It was the production also of this acid which led Strecker and other chemists to expect that alizarin would be obtained from naphthalene or some of its derivatives.

Strecker and Staedel found that by carefully acting on alizarin with nitric acid a yellow crystalline compound may be obtained, which is easily decomposed by water, nitric oxide being liberated and a red crystalline compound formed having the formula  $\text{C}_{14}\text{H}_7(\text{NO}_2)\text{O}_5$ ; as it gives with alkalis and with a solution of alum the same colours as purpurin, they consider it to be nitro-purpurin.

By the action of acetic anhydride on alizarin Perkin has obtained a *diacetyl alizarin*  $\text{C}_{14}\text{H}_6\text{O}_4(\text{C}_2\text{H}_3\text{O})_2$  crystallising in yellow needles, which when treated with nitric acid yields *nitro-alizarin*,  $\text{C}_{14}\text{H}_7(\text{NO}_2)\text{O}_4$ . The new compound crystallises in orange-yellow needles, which dissolve in caustic



alkalis with a beautiful blue colour. When nitro-alizarin is acted upon by reducing agents, it is converted into *amido-alizarin*,  $C_{14}H_7(NH_2)O_4$ , a substance crystallising from alcohol in dark chocolate-coloured needles, with a greenish metallic reflection. It may be prepared by boiling the alkaline solution of nitro-alizarin with granulated zinc until the blue colour has disappeared, and then neutralising with an acid. Its solutions are of a crimson colour.

Nitro-alizarin produces, with alumina mordants, an orange-red colour, similar to aurin, and with iron mordants a reddish purple, whilst amido-alizarin gives a purple with alumina mordants, and a bluish violet colour with iron. They both dye unmordanted silk, nitro-alizarin a clear golden colour, and amido-alizarin a purple-red.

Alizarin combines with alkalis to form salts, which are slightly soluble in alcohol but insoluble in ether. The alizarate of soda crystallises easily from alcohol; the solution of this salt has a beautiful purple colour.

Alizarin forms insoluble compounds with the alkaline earths and metallic oxides, giving salts or lakes of a variety of colours, those of the alkaline earths being violet, those of alumina red or pink, and those with the persalts of iron purple or black. Alumina has such an affinity for alizarin that it entirely removes it from its solutions.

Schützenberger states that if an ammoniacal solution of alizarin is kept for some weeks at the ordinary temperature, or is heated to  $212^{\circ}$  F. in a closed vessel, a chemical change ensues, with formation of a compound which when dry is an amorphous black mass. This he considers to be an amide of alizarin or alizaramide, and assigns to it the improbable formula  $C_{20}H_{12}O_6NH_3$ . If dissolved in hot alcohol it separates on cooling as a crystalline powder. It communicates to ether and water a beautiful violet-red hue. It yields colours to mordanted fabrics, but they are not so bright as those of madder.

Liebermann and Troschke,\* have recently examined this reaction, and find that when a *solution* of pure alizarin in aqueous ammonia is heated to about 350° F., *alizarinamide*,  $C_{14}H_9NO_3$  or  $C_{14}H_7(NH_2)O_3$ , is produced. When pure it crystallises from alcohol in beautiful brown iridescent needles, which dissolve in alkalis with a purple-blue colour. Its alcoholic solution is brownish yellow. Alizarin is regenerated when it is heated with strong hydrochloric acid to 480°. If, however, a large quantity of precipitated alizarin be heated as above with strong ammonia, crystals separate out on cooling, which, after being digested with dilute hydrochloric acid, have the composition of *alizarinimide*,  $C_{14}H_7NO_2$  or  $C_{14}H_6(NH)O_2$ . It closely resembles alizarinamide in appearance, but is scarcely soluble in ammonia or in cold alkaline solutions.

By heating a mixture of sodium alizarate with ethyl iodide in sealed tubes, at 250° F., Schützenberger obtained an ethyl derivative of alizarin, which appears to have the formula  $C_{14}H_6(C_2H_5)_2O_4$ . It is of a pale yellow colour, and is insoluble in water but soluble in alcohol.

He also obtained a benzoic derivative by heating a mixture of benzoyl chloride and alizarin to 375° F. In this reaction hydrochloric acid and a yellow compound are produced. The latter is insoluble in water but soluble in alcohol, from which it is deposited in a crystalline state. It is decomposed by a boiling solution of alkali into benzoate and alizarate of the alkali. Its formula is  $C_{14}H_6(C_7H_5O)_2O_4$ . In 1864, Stenhouse prepared a brom-alizarin by pouring an alcoholic solution of alizarin into water, adding a slight excess of bromine water, filtering and gently heating. As the alcohol evaporated the new compound crystallised out in dark-brown needles.

As already stated, Graebe and Liebermann by heating alizarin with zinc dust obtained the hydrocarbon anthra-

---

\* Deut. Chem. Ger. Bes. viii., 379.



cene, which had been discovered in 1832 by Dumas and Laurent, amongst the products formed in the destructive distillation of coal. They next attempted to reverse the process, and after considerable labour, succeeded in obtaining a product which yields all the brilliant colours for so long a time obtained only from the rubia root. This discovery of Graebe and Liebermann is one of the most interesting and important applications of chemistry to the arts that has been made of late years. Although the alizarin obtained from the madder root and that prepared artificially from anthracene give the same absorption bands in the spectrum, and when applied to mordanted fabrics produce exactly the same colours bearing the soap trial equally well, yet for some time it remained a matter of doubt as to whether the two were absolutely identical, as there were certain slight differences which were not explained until it was found that the artificial product was not pure alizarin but contained other substances. The most important of these are anthraflavic acid and anthrapurpurin. *Anthraflavic acid*, which was first noticed by Schunck, and has since been carefully examined by Perkin and by Auerbach, is isomeric with alizarin, having the composition represented by the formula  $C_{14}H_8O_4$ . To separate it, crude artificial alizarin is dissolved in boiling dilute caustic soda, and milk of lime is added until the solution becomes yellow or orange. It is then filtered from the purple alizarin lake and precipitated with hydrochloric acid. The precipitate after being washed by boiling it with alcohol is dissolved in caustic soda, and filtered from the insoluble impurities. On adding excess of barium chloride to the boiling solution and allowing it to cool, barium anthraflavate crystallises out in reddish-brown needles. The acid is readily obtained from this by decomposing it with an acid. Anthraflavic acid crystallises from alcohol in yellow silky needles, which yield a nitro compound with fuming nitric acid.



When fused with potash, anthraflavic acid yields a red substance, which dyes alumina mordants an orange-red colour.

The most convenient method of obtaining Perkin's *anthrapurpurin*\* from crude artificial alizarin is to dissolve it in dilute carbonate of soda, and agitate the solution with freshly precipitated alumina, which combines with the alizarin to form a lake, whilst the anthrapurpurin remains dissolved. On filtering and adding hydrochloric acid to the clear liquid, previously heated to boiling, the anthrapurpurin is precipitated in an impure state, being associated with a substance which gives an orange colour with alumina mordants, anthraflavic acid, &c. The impure product is washed repeatedly with boiling alcohol, then digested with boiling alcoholic soda, and the difficultly soluble sodium compound washed several times with dilute alcoholic soda, after which it is dissolved in boiling water and precipitated by barium chloride. The purple precipitate is washed with hot water, boiled with carbonate of soda, and the clear purple solution, after being separated from the carbonate of barium by filtration, is precipitated with hydrochloric acid. Anthrapurpurin,  $C_{14}H_8O_5$ , crystallises from glacial acetic acid in minute orange-coloured needles. It is soluble with difficulty in alcohol and ether, and only very slightly soluble in water. It dyes cloth, mordanted with alumina, red, and gives purple and black shades with iron mordants, but the reds are much purer and less blue than those of alizarin, whilst the purples have a bluer shade and the blacks are more intense. The fastness of the colours against soap and light are quite equal to those produced with alizarin. With Turkey red mordant it produces a brilliant scarlet, which is remarkable for its permanence.

Liebermann has succeeded in isolating from the crude alizarin a compound having the formula  $C_{14}H_8O_3$ , which

---

\* Jour. Chem. Soc., xxvi., 425.

he considers to be *monoxyanthraquinone*. It closely resembles anthraflavic acid in most of its properties, but is easily soluble in cold baryta water, whilst anthraflavic acid is nearly insoluble.

Anthracene is one of the last products passing over in the dry distillation of coal-tar, and is found most abundantly in the 10 or 15 per cent. which comes over between the temperature at which soft pitch is produced, and that at which hard pitch is formed. The quantity of anthracene in coal-tar varies greatly, but is most abundant in the tars obtained from those coals which yield most naphtha. The South Staffordshire coals give the largest quantity, whilst the Newcastle coals give very little. Its extraction can only be carried on with advantage in cold weather, as on a slight rise of temperature it becomes very soluble in the oily hydrocarbons which accompany it. The distillate above described, which at a temperature of about 40° F. is semi-fluid, is placed in a hydro-extractor, and the oily fluid separated from the solid matter. In this state it contains from 30 to 45 per cent. of anthracene.

The pasty mass is now very carefully submitted first to cold pressure, and afterwards whilst warm. It is then powdered and passed through a sieve, after which it is washed methodically with petroleum spirit, having a boiling point varying from 160° to 195° F., when it is again submitted to hydraulic pressure. After being resublimed it is in a fit state for the manufacture of alizarin.

Pure anthracene presents itself under the form of fluorescent transparent crystals, consisting of four or six-sided plates, which have a peculiar very pale blue hue when seen by transmitted light, changing to pale violet by reflected light. Its preparation is a very tedious process, for which as well as for its tests (differing only in degree from those for the commercial article), we must refer the reader to the beautiful *résumé*, on anthracene

and its derivatives, by M. Emile Kopp, in the *Moniteur Scientifique*.\*

When allowed to crystallise slowly from alcohol it forms oblique prisms with regular bases belonging to the monoclinic system; it begins to volatilise at a temperature of  $212^{\circ}$  F., giving off vapours which have a peculiarly disagreeable odour, and are very irritating to the throat and eyes. It melts at  $410^{\circ}$  F. and boils at a temperature between  $610^{\circ}$  and  $630^{\circ}$  F., when it sublimes in crystals, very similar to those described above, the vapours of which are so dense that the crystals condense on the top and in the neck of the retort. This latter fact suggested to the author that a much larger yield of anthracene might be obtained if during the distillation steam superheated to a temperature of between  $600^{\circ}$  and  $700^{\circ}$  F. were blown through the oily mass. The results obtained were very satisfactory.

Anthracene is only slightly soluble in alcohol, but rather more so in ether and bisulphide of carbon. It is more soluble in hot benzene, but less in cold. Petroleum boiling between  $160^{\circ}$  and  $195^{\circ}$  F., dissolves less than benzene.

In the cold, alcohol dissolves .6 per cent., benzene .9, and bisulphide of carbon 1.7 of anthracene. Alkalis even when boiling have no action upon it. Anthracene dissolves in concentrated sulphuric acid with a green colour, and forms conjugated monosulpho or bisulpho-anthracenic acid, according to the temperature employed. Chlorine and bromine give rise to substitution products. Nitric acid acts on it with great violence, with formation of anthraquinone, dinitro-anthraquinone, and other compounds, according to the temperature and proportion of the substances taken. With picric acid anthracene forms a compound, crystallising in very bright ruby-red needles, which, by the aid of the

---

\* Vol. xiii., p. 531.



microscope are seen to be prisms. To prepare it, a saturated solution of picric acid in water at 80° F. is mixed with a saturated solution of anthracene in boiling alcohol; on cooling, the compound is deposited in the crystalline state. It is rapidly decomposed by an excess of alcohol into picric acid and anthracene, the solution assuming a yellow tint. This reaction can be employed to distinguish anthracene from naphthalene and other hydrocarbons, naphthalene under similar circumstances forming a compound which crystallises in fine golden-yellow needles, whilst chrysene gives rise to clusters of very small yellow needles.

Another characteristic of anthracene observed by Fritzsche is its behaviour under the microscope with a solution of binitro-anthraquinone in benzene. In this reaction fine rhomboidal scales having a beautiful pink colour are formed, the purity and brilliancy of the colour of course depending on the purity of the anthracene.

Before leaving this subject, it may be stated that Berthelot\* has described several reactions in which anthracene is formed; as by the action of heat on other hydrocarbons, or by passing the vapours of ethylene, styrolene, and benzene through a porcelain tube heated to a bright red heat.

The method by which Messrs. Graebe and Liebermann first succeeded in obtaining artificial alizarin consisted in transforming anthracene  $C_{14}H_{10}$  into anthraquinone  $C_{14}H_8O_2$  by the action of nitric acid, which removes two equivalents of hydrogen from the hydrocarbon and adds two of oxygen. The anthraquinone thus obtained is acted on by bromine which replaces two equivalents of hydrogen and gives rise to bibromanthraquinone  $C_{14}H_6Br_2O_2$ . This compound when fused with hydrate of potash yields bromide of potassium and alizarin according to the following equation:



This process, although important from a scientific point of

---

\* Bul. Soc. Chim., vii., 274.

view, could not be carried out on a practical scale, being much too costly; a cheaper method was therefore looked for.

The best laboratory process for the production of anthraquinone consists in making separate solutions of anthracene and chromic acid in glacial acetic acid, and gradually adding the chromic acid solution to the anthracene until the liquid, which is at first bright green, assumes a slightly yellow tinge, showing that there is chromic acid in excess. On the liquid being allowed to cool needles of anthraquinone crystallise out, the amount of which may be increased by adding water to the solution. The crude substance is collected on a filter, washed, dried, and sublimed, when it yields yellow crystals of pure anthraquinone, the formula of which is, as stated above,  $C_{14}H_8O_2$ .

It is more economical to substitute sulphuric acid for acetic acid, and bichromate of potash or peroxide of manganese for the chromic acid, which is the method adopted in the patented process.

The crystalline form which anthraquinone assumes depends on the exact method and temperature employed in its sublimation. It is insoluble, or only very slightly soluble, in alcohol, ether, and benzene. It melts at  $520^{\circ}$  F., and distils at a higher temperature without decomposition. Its power of resisting the action of chemical reagents is very characteristic.

If anthraquinone be heated with hydrate of potash in a silver crucible to a temperature of  $480^{\circ}$  F. the mass becomes blue, as if alizarin were produced, but on the addition of water it loses its colour and the anthraquinone reappears in the form of colourless flocks. Wartha\* finds that when caustic potash is added to an alcoholic solution of anthraquinone the colourless solution quickly assumes a yellowish tinge, and if the application of heat be continued

---

Ann. Chem. Pharm. clxi., 305.

until the whole of the alcohol is given off and the mass fuses, it becomes first greenish and then takes the peculiar violet-purple tint characteristic of the presence of alizarate of potash; in fact from this mass he succeeded in obtaining alizarin in small quantity. He observed that the addition of chloride of tin greatly facilitates the transformation, and that if the anthraquinone be mixed with twice its weight of ethylate of sodium (a product obtained by the action of sodium on anhydrous alcohol) the same effect is produced. These observations of Wartha are interesting as they show that alizarin can be produced directly from anthraquinone without previously converting it into bisulpho-anthraquinonic acid.

Anthraquinone may be boiled with sulphuric acid of specific gravity 1.4, without alteration. With a mixture of concentrated nitric and sulphuric acids it is converted into binitro-anthraquinone  $C_{14}H_6(NO_2)_2O_2$ . Anthraquinone dissolves in cold concentrated sulphuric acid, and if the mixture be strongly heated for some time bisulpho-anthraquinonic acid  $C_{14}H_8O_2 \cdot 2SO_3$  is formed. When this bisulpho-anthraquinonic acid is heated at  $360^\circ F.$  with an excess of potassium hydrate, it gives rise to sulphite and alizarate of potash, as shown in the following equation:—



There have been several patents taken out for the manufacture of artificial alizarin. The specification of Messrs. Caro, Graebe, and Liebermann, here given, was the first which was taken out in England, and enters more fully into detail than any of the others. The provisional specification was dated June 25th, 1869.

“Our invention is carried into effect by means of either  
“of the two processes, which we will proceed to describe.

“In the one process we proceed as follows:—We take  
“about one part by weight of anthraquinone and about  
“three parts by weight of sulphuric acid of about the



"specific gravity of 1.848, and introduce the same into a  
"retort, which may be made of glass, or of porcelain, or of  
"other material not easily acted upon by sulphuric acid,  
"and the contents are then to be heated up to about two  
"hundred and sixty degrees centigrade, and the tempera-  
"ture is maintained until the mixture is found no longer to  
"contain any appreciable quantity of unaltered anthra-  
"quinone. The completion of this desired operation may  
"be ascertained or tested by withdrawing a small portion  
"of the product from time to time and continuing the  
"operation at the high temperature until such product  
"upon being diluted with water is found to form a sub-  
"stantially perfect solution, thereby indicating that the  
"anthraquinone has become either entirely or in greater  
"part converted into the desired product. The results of  
"this operation are then allowed to cool and are diluted  
"with water: we then add carbonate of lime in order to  
"neutralize and remove the excess of sulphuric acid con-  
"tained in the solution; the mixture is then filtered, and to  
"the filtrate carbonate of potash or carbonate of soda, by  
"preference in solution, is to be added until carbonate of  
"lime is no longer precipitated; the mixture is then filtered  
"and the clear solution is evaporated to dryness, by which  
"means the potash or soda salts of what we call the sulpho-  
"acids of anthraquinone are obtained and which are to be  
"treated in the following manner:—We take about one  
"part by weight of this product and from two to three  
"parts by weight of solid caustic soda or potash; water  
"may be added or not, but by preference we add as much  
"water as is necessary to dissolve the alkali after admix-  
"ture; we heat the whole in a suitable vessel, and the  
"heating operation is continued at a temperature of from  
"about one hundred and eighty degrees to about two  
"hundred and sixty degrees centigrade for about one hour  
"or until a portion of the mixture is found upon with-

“drawing and testing it to give a solution in water, which  
“being acidulated with an acid, for example sulphuric acid,  
“will give a copious precipitate of the colouring matters.  
“The heating operation having been found to have been  
“continued for a sufficient time the resulting products are  
“then dissolved in water, and we either filter or decant the  
“solution of the same, from which we precipitate the  
“colouring matters or artificial alizarin by means of a  
“mineral or organic acid, such, for example, as sulphuric  
“or acetic acid. The precipitated colouring matters thus  
“obtained are collected in a filter or otherwise, and after  
“having been washed may be employed for the purposes of  
“dyeing and printing either in the same way as prepara-  
“tions of madder are now used, or otherwise.

“In carrying out our other process we proceed as follows:  
“We take about one part by weight of anthracene and  
“about four parts by weight of sulphuric acid of specific  
“gravity of about 1.848, and the mixture being contained  
“in a suitable vessel is heated to a temperature of about  
“one hundred degrees centigrade, at which temperature it  
“is to be maintained for the space of about three hours;  
“the temperature is then to be raised to about one hundred  
“and fifty degrees centigrade, which temperature is to be  
“maintained for about one hour or until a small portion of  
“the product when submitted to the subsequent processes  
“herein-after described is found to produce the desired  
“colouring matters; we then allow the result obtained by  
“this operation to cool, and dilute it with water, by prefer-  
“ence in the proportion of about three times its weight.  
“To the solution thus obtained we add for every part of  
“anthracene by weight which had been employed in the  
“previous operation about from two to three parts by  
“weight of peroxide of manganese, preferring to employ an  
“excess, and we boil the whole strongly for some time, and  
“in order fully to ensure the desired degree of oxidation

“the mixture may be subsequently concentrated and by  
“preference be evaporated to dryness and the heat be con-  
“tinued until a small portion of the oxidised product when  
“submitted to the subsequent processes herein-after de-  
“scribed will produce the desired colouring matters. We  
“then neutralise and remove the sulphuric acid contained  
“in this mixture, and at the same time precipitate any  
“oxides of manganese which may be held in solution by  
“adding an excess of caustic lime which we use by prefer-  
“ence in the form of milk of lime, and we add the same  
“until the mixture has an alkaline reaction. We then filter  
“and add to the filtrate carbonate of potash or soda until  
“there is no further precipitation of carbonate of lime.  
“The solution is then filtered and evaporated to dryness,  
“and we thus obtain the potash or soda salts of what  
“we call the sulpho-acids of anthraquinone.

“In effecting the conversion of the oxidised products  
“thus obtained into colouring matters, or into what we call  
“artificial alizarin, we proceed as follows:—We take one  
“part by weight of this product and from two to three  
“parts by weight of solid caustic soda or potash, and water  
“may be added or not, but by preference we add as much  
“water as is necessary to dissolve the alkali. After admix-  
“ture we heat the whole in a suitable vessel and continue the  
“heating operation at a temperature from about one hun-  
“dred and eighty degrees to about two hundred and sixty  
“degrees centigrade for about one hour, or until a portion of  
“the mixture is found to give a solution in water which upon  
“acidulation with an acid, for example sulphuric acid, is  
“found to give a copious precipitate of the colouring  
“matters. The heating operation having been found to  
“have been continued for a sufficient time we then dissolve  
“the product in water, and either filter or decant the solution  
“of the same, from which we precipitate the colouring  
“matters or artificial alizarin by means of a mineral or



"organic acid, such, for example, as sulphuric or acetic acid. The precipitated colouring matters thus obtained are collected on a filter or otherwise, and after having been washed may be employed for the purposes of dyeing and printing either in the same way as preparations of madder are now used or otherwise. Instead of acting upon anthracene by means of sulphuric acid of the density before mentioned, fuming sulphuric acid may be employed, but we prefer to use the ordinary acid, as before described.

"In order to effect the process of oxidation before referred to, other oxidising agents may be used in place of the peroxide of manganese before mentioned, such, for example, as peroxide of lead, or chromic, nitric, or other acids capable of effecting the desired oxidation may be employed."

Mr. W. H. Perkin also took out a patent only one day later, his process being exactly the same in principle.

MM. Brœnner and Gutzkon patented in France, in May, 1869, a process differing from the two already mentioned, of which the following is an outline:—One part of anthracene is heated with two parts of nitric acid of specific gravity 1.3 to 1.5. The anthraquinone thus produced is washed and dissolved at a moderate heat in sulphuric acid. Mercuric nitrate is now added, which converts the anthraquinone into alizarin. The mass thus formed is dissolved in an excess of alkali, which precipitates the oxide of mercury and retains the colouring matters in solution. The alkaline liquor is decanted and neutralised with sulphuric acid, and the precipitate thus formed is washed and collected. If not quite pure the treatment with alkali must be repeated.\*

A large quantity of artificial alizarin is now manufactured in England by Perkin's process, and it is used as a substi-

---

\* For complete specification see *Moniteur Scientifique*, vol. xi., p. 865.

tute for madder and extract of madder in Turkey red dyeing and topical styles.

On the continent the largest manufacturers are Messrs. Gessert Frères, of Ebelfert; Messrs. Meister, Lucius, and Co., of Höchst, near Frankfort; and the Badische Anilin und Soda Fabrik, Mannheim.

According to Boettger, a fine orange colour can be obtained from anthracene by heating slowly to about 70° F., one part of anthraquinone with sixteen times its weight of a mixture of sulphuric acid of specific gravity 1.84, and nitric acid of specific gravity 1.50. When the anthraquinone is dissolved, the mixture is immediately poured into a large quantity of water, and a nitrogenised compound separates in voluminous yellowish-white flakes. These are collected and acted on by a solution of protoxide of tin in alkali, which dissolves the flakes, assuming at the same time a magnificent emerald green tint. On boiling this solution the anthracene orange is precipitated as a beautiful cinnabar red powder, having the formula  $C_{14}H_6N_2O_6$ . When heated to a temperature of 500° F. it sublimes in fine red needles, which have a green iridescence. Its best solvents are chloroform, ether, alcohol, and wood spirit.

Colours somewhat similar to alizarin have been prepared from naphthalene, but they will not stand a soaping process. The first of these was obtained by Roussin in 1861, who gave it the name of naphthazarin. Its formula is  $C_{10}H_4O_4$ . For some little time after its discovery it was believed to be alizarin; in fact, Dumas, then president of the academy of sciences, introduced it to that assembly as alizarin. It is prepared by the following simple process.

Five hundred grammes of concentrated sulphuric acid are mixed with one hundred of dinitronaphthalene in a large porcelain capsule and gradually heated to 350° F. The source of heat is then removed and one hundred grammes of crystallised protochloride of tin or granulated zinc is gradually



added in very small quantities at a time. If too much of the reducing agent be added at one time, the temperature rises rapidly and the operation is spoiled. For if the heat reaches  $400^{\circ}$  F. the colour is destroyed, whilst at  $480^{\circ}$  F. the whole mass becomes carbonised. The product resulting from this reaction is allowed to cool. Hot water is then added, the mixture boiled, and rapidly filtered. A beautiful purple-red liquor is obtained, from which, on cooling, the naphthazarin separates in the form of small flakes or crystals. One hundred parts of binitronaphthalene yield only five parts of naphthazarin.

This colouring matter dissolves in alkalis, but its solution is more violet than that of purpurin, and not so blue as that of alizarin. On fabrics with alumina mordants it gives a red, more or less purple, and with iron mordants a greenish-grey.

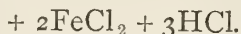
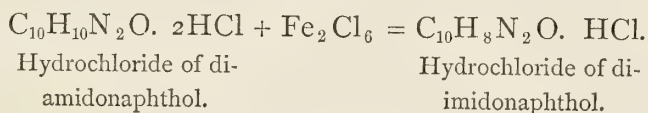
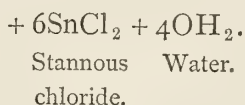
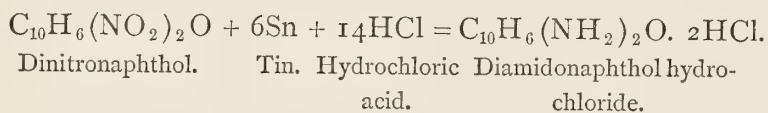
A second product called oxynaphthalic acid, having the formula  $C_{10}H_6O_3$ , was prepared by Martius and Griess in 1866. Many eminent chemists thought at that time that alizarin was oxynaphthalic acid, and were occupied in attempting to prepare this compound. When it was obtained, however, it was found to differ considerably from alizarin.

The process followed by Martius and Griess has since been considerably improved by Graebe and Ludwig. Their method is as follows :

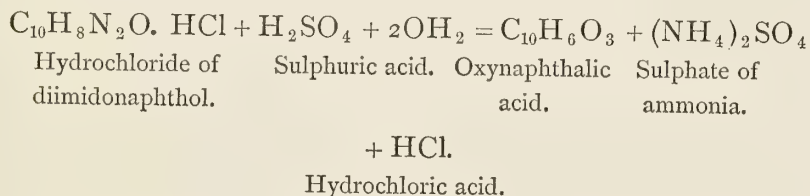
One part of dinitronaphthol, two parts of granulated tin, and seven and a half parts of concentrated hydrochloric acid are heated in a large capsule until a violet colour is produced. As soon as this appears the source of heat is removed, that generated by the chemical action being sufficient to complete the transformation. Water is then added, and plates of zinc are placed in the solution, whereby the tin is thrown down and replaced by the zinc, which dissolves. The precipitated metal is removed by filtration, and



perchloride of iron is added to the filtrate as long as any precipitate is produced. This is collected on a filter and washed with cold water. After being dissolved in boiling water and allowed to cool, prisms or rhomboidal tables separate which are red by transmitted light and green by reflected light. The two following equations show the reactions :



To complete the transformation, the crystals of hydrochloride of diimidonaphthol are boiled for an hour with a quantity of sulphuric acid of such strength that its boiling point is 250° F. The following reaction ensues :



The solution thus obtained is boiled with carbonate of baryta, which precipitates the sulphuric acid, leaving the oxynaphthalic acid in solution combined with baryta. On the addition of hydrochloric acid to this solution the oxynaphthalic acid is precipitated in the form of small needles, which are only slightly soluble in water even when boiling, and which can be sublimed in slender needles very similar to those of sublimed alizarin.

This acid differs from alizarin in yielding, with ammonia, a yellowish-red colour instead of a bluish-violet; moreover, it combines with ammonia to form a well-defined salt. The precipitate which it gives with the various metallic salts are quite different from those obtained with alizarin. It imparts a yellow colour to silk and wool, but does not yield any colour to alumina mordants.

*Purpurin*.—Like alizarin, this substance forms crystalline compounds with the alkalis, that of soda crystallising in well-defined elongated prisms. With salts of alumina it gives a red-lake free from all blue tint, and with persalts of iron purples and blacks. It forms an amido compound similar to that obtained from alizarin. This was discovered by Stenhouse in 1864, who found that a solution of purpurin in ammonia when allowed to stand for several weeks loses its power of dyeing mordanted cloth. On neutralising the solution, a dark-red crystalline precipitate is produced, which is soluble in a large quantity of boiling water, and separates again on cooling in long crimson needles, which have a deep green iridescence by reflected light. They are soluble in alcohol. Its formula appears to be  $C_{14}H_9NO_4$  or  $C_{14}H_7(NH_2)O_4$ . Schützenberger has also prepared *purpurinamide* by heating purpurin with ammonia in sealed tubes to the temperature of boiling water.

Purpurinamide, as shown by Stenhouse, dissolves freely in nitric acid of specific gravity 1.5 at a temperature of  $212^{\circ}$  F., and yields on cooling magnificent scarlet crystals, which somewhat resemble chromate of silver in appearance, but have a brighter colour. They are insoluble in water, ether, and bisulphide of carbon, but are slightly soluble in alcohol.

No crystalline compounds have as yet been obtained by the action of bromine on purpurin.

When investigating the hydride of alizarin, Bolley

observed that purpurin underwent a similar change to the alizarin, the red alkaline solution of purpurin passing into orange, and finally to a brownish-yellow, when treated with reducing agents. In operating with equal care, as in the case of alizarin, to prevent the absorption of oxygen from the atmosphere, he obtained a flocculent precipitate which is easily sublimed in long golden-yellow needles. There appears to be no difference in composition between the body before and after sublimation. The formula assigned to it by Bolley is  $C_{20}H_{16}O_5$  (?), who considers purpurin to be  $C_{20}H_{12}O_7$  (?). The hydride dissolves readily in alcohol or ether, but is less soluble in water or benzene. These solutions keep very well when exposed to the atmosphere, but its alkaline solution gradually absorbs oxygen and acquires a red colour. It is also soluble in a solution of alum. Bolley also states that if purpurin is heated in sealed tubes to a temperature of  $400^{\circ}$  F. it forms a carbonaceous mass from which water extracts alizarin. This conversion can also be effected by heating the purpurin with water in sealed tubes to the same temperature. Under the influence of the high temperature the purpurin loses oxygen and is converted into alizarin. Rosenstiehl,\* on the contrary, finds that *pure* purpurin yields no alizarin under these circumstances, and attributes the supposed transformation observed by Bolley to the use of impure purpurin.

Professor Stokes, of Cambridge, has devised a most elegant method of discovering and distinguishing mere traces of these colouring principles. The following is a clear and concise description of his useful and practical process, which is inserted as an appendix to Schunck's paper on madder in the Journal of the Chemical Society:—†

---

\* Compt. Rend., lxxix., 680.

† Vol. xii., p. 219.



The optical characters of purpurin are distinctive in the very highest degree; those of alizarin are also very distinctive. The characters here referred to consist in the mode of absorption of light by certain solutions of the bodies, and occasionally in the powerful iridescence of a solution. They are specially valuable because they are independent of more than a moderate degree of purity of the specimens, and require no apparatus beyond a test-tube, a slit, and a small prism, an instrument which ought to be in the hands of every chemist.

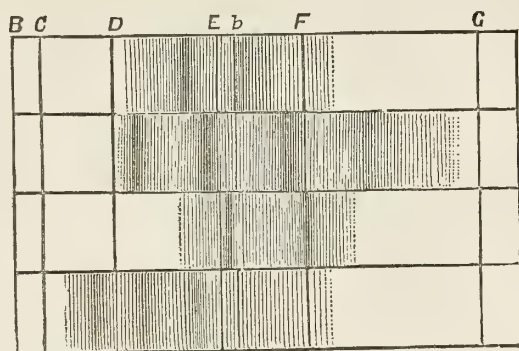
*Alkaline solution of purpurin.*—If purpurin be dissolved in a solution of carbonate of potash or soda (it is easily decomposed by caustic alkalis), the solution obtained absorbs with great energy the green part of the spectrum. In this and similar cases it is necessary to take care either to use a sufficiently small quantity of the substance or else to dilute sufficiently the solution, or view it through a sufficiently small thickness; otherwise a broad region of the spectrum is absorbed, and the peculiar characters of the substance depending on its mode of absorbing light are not perceived. If the solution be contained in a wedge-shaped vessel, the effect of different thicknesses is seen at a glance; but a test-tube will answer perfectly well, if two or three different degrees of dilution be tried in succession. When the light transmitted through an alkaline solution of purpurin of suitable strength, after being limited by a slit, is viewed through a prism, two remarkable dark bands of absorption are seen about the green part of the spectrum, comprising between them a band of green light, which, though much weakened in comparison with the same part of the unabsorbed spectrum, is bright compared with the two dark bands, which latter in a sufficiently strong solution appear perfectly black. The places of the dark bands, estimated with reference to the principal fixed lines of the spectrum, are given in the figure.

Fig. 1.—Solution of purpurin in carbonate of soda or potash, or in alum-liquor.

Fig. 2.—Solution of purpurin in bisulphide of carbon.

Fig. 3.—Solution of purpurin in ether.

Fig. 4.—Alkaline solution of alizarin.



*Solution in a solution of alum.*—This solution has the same peculiar mode of absorption, and will serve equally well for it. But it has the further property of being eminently iridescent, which the alkaline solution is not at all. The iridescent light is yellow, but ordinarily appears orange from being seen through the fluid. The difference between the alkaline and alum liquor solutions as to iridescence does not depend on the acid reaction of the latter, but on the alumina. A solution, exhibiting to perfection the peculiar properties of the alum liquor, may be obtained by adding to a solution of purpurin in carbonate of soda a solution of alum to which enough tartaric acid has been added to prevent precipitation when carbonate of soda is added, which must be done previous to mixing, and in this case the solution is obtained at once and in the cold. This forms a very striking reaction in a dark room, according to the method described in the Philosophical Transactions for 1853, p. 385, with the combination solution of nitrate of copper and a red ( $\text{Cu}_2\text{O}$ ) glass. Some other colourless oxides, besides alumina, develop in this manner iridescence although in a less degree.

*Solution in bisulphide of carbon.*—This solution gives the highly characteristic spectrum exhibiting four bands of absorption, of which the first is narrower than the others, and the fourth is not at all conspicuous, hardly standing out from the general absorption which takes place in that



region of the spectrum. The second and third bands are the most conspicuous of the set.

*Solution in ether.*—This gives the characteristic spectrum exhibiting two bands of absorption. The solution is iridescent, but not enough so to be perceptible by common observation.

The spectra of the solutions of purpurin in other solvents might be mentioned, but these are more than sufficient. From an optical point of view purpurin is remarkable for the general similarity of character combined with diversity as to detail, which its various solutions exhibit as to their mode of absorbing light.

*Alkaline solution of alizarin.*—The solution of alizarin in caustic or carbonate of potash or soda, or in ammonia, exhibits on analysis a characteristic spectrum, having a band of absorption in the yellow, and another narrower one between the red and the orange. There is a third very inconspicuous band at E in the spectrum, almost lost in the general darkening of that part.

*Other solutions.*—The solution of alizarin in ether or bisulphide of carbon shows nothing particular. There is a general absorption of the more refrangible parts of the spectrum, but there are none of those remarkable alternations of comparative transparency and opacity which characterise purpurin. Alizarin is hardly soluble in alum liquor; and in the case of the red solution, of mixed alizarin and verantin, mentioned by Dr. Schunck at page 451 of the Philosophical Transactions for 1851, the absence of the remarkable absorption bands and the absence of iridescence show instantly and independently of each other that it is distinct from purpurin.

*Optical detection of purpurin and alizarin.*—The characters of these substances are so marked that I do not know any substance with which either of them could be confounded, even if we restricted ourselves to any one of the solutions yield-



ing the peculiar spectra. Not only so, but these properties enable us to detect small quantities, in the case of purpurin the merest trace, of the substance present in the midst of a quantity of impurities. In the case of purpurin a solution of alum is specially convenient for use, because the impurities liable to be present do not, with this solvent, absorb the part of the spectrum in which the bands occur. In this way I was able, though operating on only a very minute quantity of the root, to detect purpurin in more than twenty species of the family *rubiaceæ*, which were examined with this view, comprising the genera *Rubia*, *Asperula*, *Gallium*, *Crucianella*, and *Scherardia*. The detection of alizarin by means of the characters of its alkaline solution is much less delicate, because many of the impurities liable to be present absorb the part of the spectrum in which all but the least refrangible of the absorption-bands occur; and as this band is not that which corresponds to the most intense absorption, a larger quantity of the substance must be present in order that the band may be perceived.

### CHAPTER III.

#### MADDER.—CONTINUED.

In the preceding chapter the colour-giving principles contained in madder roots have been described, and also the various compounds isolated from them by chemists, as well as the artificial production of alizarin, which is the most important of the latter. It will now be necessary to give a brief account of Turkey red, and madder dyeing, and the manufacture of the principal preparations of madder, such as garancin, pinkoffin, *fleurs de garance* and the extracts of madder. The various processes employed for obtaining alizarin and purpurin on a commercial scale will then be noticed, and lastly the methods employed for testing madders and garancins.

The principal use of madder is to dye cotton cloth of different shades of red, of which by far the finest hue is that called in this country and on the continent by the name of Turkey or Adrianople red—one of the most durable colours known. It seems highly probable that the method of dyeing this tint—the characteristic of which consists in previously impregnating the goods with an oily or fatty substance—originated in India, where, as travellers affirm, the natives have been wont, from time immemorial to steep the yarns which they intend to dye in liquids containing fatty matter, such for example as milk. It was not, however, until after it had made its way into other parts of Asia, and become known in the countries of the Levant, undergoing at the same time important modifications, that this art was first

introduced into France, towards the middle of the last century. In 1747, Messrs. Ferquet, Goudard, and D'Haristoy brought a party of Greek dyers into that country, and formed two establishments, one at Darnétal, near Rouen, and the other at Aubenas, in Languedoc. Nine months later, a person named Flachat, who had long resided in the Ottoman Empire, brought over workmen with whom he formed at St. Chamont, near Lyons, a third establishment for the dyeing of Adrianople red, so called from the high celebrity then enjoyed by the productions of that city. But as these foreigners could not long keep their art secret, they soon had numerous imitators; and in 1765, the French government, convinced of the value and importance of this method of dyeing, made the processes known to the public. Many establishments were formed in various parts of the country; but it appears that the only successful ones for some years were those at Rouen. From these parts the Turkey red dye gradually made its way into Alsace, Switzerland, Great Britain, and different parts of Germany. At first the cotton was only dyed in the yarn; and it was not until 1810 that the cloth itself was dyed directly of this colour at the establishment of Messrs. Kœchlin, Mulhausen, and that of L. Weber.

It is stated by the late Dr. Thomson, of Glasgow, and other authorities, that the first Turkey red works in Great Britain were established in that city about ninety years ago by a M. Papillon. It appears, however, from a paper on the art of dyeing, read before the Literary and Philosophical Society of Manchester, by M. Thomas Henry in 1786, and quoted by Mr. Baines in his *History of the Cotton Manufacture*, that M. Borelle, another Frenchman, introduced the art of dyeing Turkey red at Manchester, probably some years previous to its introduction at Glasgow, and that he obtained from Government a grant for the disclosure of his plans, as M. Papillon did afterwards from the commissioners



and trustees for manufactures in Scotland ; but the method of the latter obtained the most decided success. It was in the year 1783, that Mr. David Dale and Mr. George Macintosh—father of the late Mr. Charles Macintosh, the inventor of the well-known waterproof fabrics—engaged Papillon, who was a dyer at Rouen, to settle in Glasgow, and he there founded and carried on in partnership with Mr. Macintosh the celebrated Turkey red business now conducted by the firm of Messrs. Monteith and Co. The period having expired in 1803, when the process was to be divulged, the commissioners and trustees above mentioned laid a complete account of it before the public. Since that period Turkey red dyeing has been conducted in Glasgow, and also in Lancashire on a very extensive scale.

There are several processes followed for producing Turkey red at the present time, but the operations are so numerous, and success so much depends on matters of detail in the carrying out of the various operations, that it is impossible to describe with sufficient minuteness in a work like the present all the precautions requisite to produce colours equal to those obtained by Messrs. Steiner and Co., and several other firms in Manchester and Glasgow. The following, however, is an outline of the process:

A thousand pounds of calico are steeped in tepid water for a day or two, to remove either by solution or fermentation the greater part of the size used for stiffening the warp. This operation can be much shortened by adding a small quantity of malt liquor to facilitate the transformation of the starch into glucose. The pieces are next boiled in a keir, with a weak solution of carbonate of soda having a specific gravity of 1.01, after which the goods are oiled by padding them in a mixture of 580 lbs. of rancid Gallipoli oil, or what is called by the French *huile tournante*, and 150 gallons of water in which is dissolved 10 lbs. of a mix-

ture of potassium and sodium carbonate. To this mixture some dyers still add sheep or cow dung, believing that the azotised mucilaginous substance called by Morin *bubulin*, materially contributes to the fixing of the fatty acids on the fabric. The pieces are now exposed to the atmosphere until they feel dry, when they are placed in a stove heated to 140° F. After twelve hours they are taken out and the padding operation repeated two or three times, according to the intensity of the colour required. The pieces are next steeped for twenty-four hours in a bath containing carbonate of soda, to remove the fatty acids which have not been fixed in the fibre. The liquid is pressed out, and is called *old white liquor*. It is employed again in the oiling operations. The goods are carefully rinsed out, and are ready for the *mordanting* process, which consists in passing the pieces at a temperature of 150° through a bath composed of 30 gallons of water, 10 lbs. of ground gallnuts or sumach, and 16 lbs. of alum. They are then hung for two days in a stove, the temperature of which is maintained at 140° F., and afterwards passed in a hot chalk bath. They are then thoroughly washed and are ready for the dyebeck. (Madder, which was formerly exclusively employed for this work, is now almost entirely replaced by garancin and by artificial alizarin.) The dyeing is performed by introducing ten pieces into a beck containing 300 or 400 gallons of water; 17 to 20 lbs. of madder, or 3 to 5 lbs. of garancin for each piece are added and steam is introduced, the heat being gradually raised during an hour and a half to 180° F., it is then rapidly carried to near the boiling point and maintained at that temperature for an hour. The pieces are taken out, thoroughly washed by a washing machine, passed a second time through the mordanting liquor, the chalk bath, and the washing process, and again placed in the dyebeck. The red thus produced is dark and dull, as in the accompanying sample.



TURKEY RED AS DYED.

To brighten it, it is submitted to three clearing processes, which are performed in closed boilers two-thirds filled with water. For the first process about 6 lbs. of soap and  $1\frac{1}{2}$  lbs. of carbonate of potash are added, and the liquor kept boiling for eight hours.

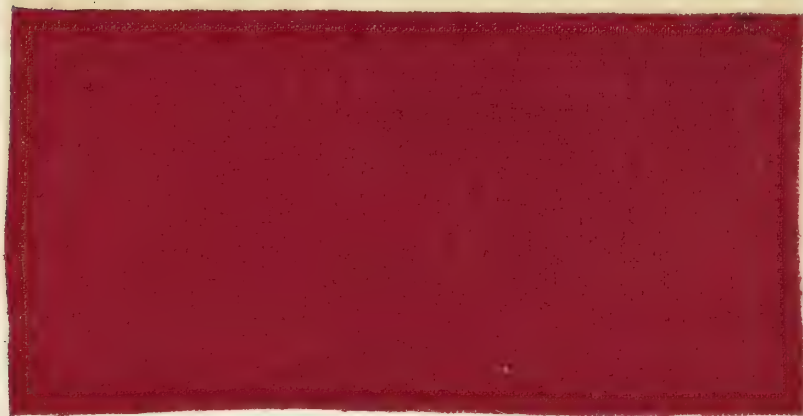


TURKEY RED AFTER FIRST CLEARING.

The pieces are again washed and boiled. This time with 6 lbs. of soap and 7 oz. of chloride of tin. After this pro-



cess has been repeated, the goods are exposed for some time to the atmosphere, passed through a hot bran bath, washed, and dried.



## TURKEY RED FINISHED.

We are indebted to the kindness of Messrs. Steiner and Co., of Church, near Accrington, for these samples of Turkey red.

The same process is followed to produce Turkey red upon yarn. Of late years, also, very fine purple-dyed yarns have been produced by following the process above described—but dipping the yarn in a solution of nitrosulphate of iron after the oiling processes.

Several chemists, among whom may be cited Persoz, Schützenberger, Kœchlin, and Jenny have tried to give a rational explanation of the above operations, and to find out why cotton treated by this method is dyed a red which is faster and more brilliant than can be obtained by any other process. One thing is certain, that fatty matters are essential, and the oil must be in such a state that on being mixed with carbonate of soda it will give an emulsion, or white milky fluid. An oil possessing this property is called by the French *huile tournante*. A sweet olive oil

does not produce an emulsion, and cannot be used with advantage, but common Gallipoli gives favourable results.

It is believed by many chemists and Turkey red dyers that the oil must undergo a certain amount of oxidation, and several patents have been taken out to effect this. It is doubtful, however, whether oils treated by these processes have to any extent replaced old Gallipoli.

It seems probable that the explanation given by Pelouze in 1836 is the real one. He found that the oily matters contained in a seed or berry could be kept sound for almost any length of time if the seed were unbroken, but if it were crushed, a peculiar ferment existing in the seed came in contact with the fatty matters, and acting on them, converted them into glycerin and fatty acids. He proved that in the case of olives this change takes place in a few hours after the berries are crushed, and that the amount of free fatty acids is largely increased if they are allowed to stand for any length of time.

The best qualities of olive oil are obtained by pressing the berries, first at natural temperatures, and then between hot plates, by this means the oil gets separated from its ferment at once. At Gallipoli and the surrounding country, the berries as soon as gathered are thrown into heaps and allowed to ferment. By this process a much larger yield of oil is obtained, but of inferior quality, owing to its partial decomposition.

The correctness of these views is corroborated by the fact that Mr. Steiner obtained very good Turkey reds, when, at the suggestion of Pelouze he substituted for the usual Gallipoli oil, oleic acid obtained in the manufacture of stearin candles.

No doubt can remain that great progress is still being made in the production of this class of goods, especially in shortening the time required for the operations. At the exhibition of 1867, M. Cordier, of Bapaume, near Rouen,

satisfied the jury that he could obtain a first-class Turkey red on cotton yarns in five days.

Artificial alizarin is now being substituted for garancin in the production of Turkey red, and some printers are using large quantities of the artificial product. M. Armand Müller states that a red similar in tint and purity to Turkey red may be obtained by direct printing with artificial alizarin in the following manner.

The pigment, in a pasty form, and having 25 per cent. of dry material, is dissolved in boiling spirit in the proportion of one to five, and immediately mixed with a concentrated solution of chloride of aluminium, of which the pure chloride is to the weight of the colouring matter as one to three. The liquid is thickened with a little tragacanth, and for every half litre of this mixture 30 cc. of a solution composed of the best olive oil (fifteen parts), of sulphuric acid (one part), and spirit (fifteen parts), is stirred in. This solution must be as thin as possible, but must be thick enough to withstand the capillarity of the cloth. The cotton cloth with which this colour is to be used is first impregnated with a solution of acetate of alumina of about 8° Baumé, and after drying and two days ageing is taken through a soap bath containing 30 grms. of Marseilles soap to the litre of water, then well washed out and dried.

The cloth printed with the above mixture is now exposed to strongly ammoniacal steam at a moderately high pressure, taken through a weak soap bath, washed in a stream, and taken through the following series of liquids:—  
1. cold nitric acid, 3 cc. to 1 litre of water; 2. washed in stream; 3. cold nitric acid, 5 cc. to 1 litre of water; 4. tin salt,  $\frac{1}{2}$  gm. to 1 litre of water at 90° F.; 5. washed in stream; 6. liquor of Javelle, 15 cc. of 8° Baumé to 1 litre of water, cold; 7. thorough washing. The colour is now thoroughly developed, and behaves to light, air, and soap like ordinary Turkey red. In preparing the chloride of



aluminium (by the addition of chloride of barium to sulphate of alumina) it is absolutely necessary to avoid an excess of the barium salt.

The art of printing calico with madder was known to the Egyptians and the countries of the East from time immemorial, and we find on the fabrics wrapped round some of the mummies designs in red and purple, which have been produced by combinations of the colour-giving principles of madder with alumina and iron mordants. In Persia and India the art had attained a certain degree of perfection, and up to the beginning of the 18th century printed fabrics called chintz were imported from those countries. A very heavy duty was, however, put on them in 1700, and their importation entirely prohibited in 1720. Although this was altered in 1774, a duty of 3½d. per square yard was imposed on all printed calicos, whether imported or made in England, and it was not until 1831 that this duty was repealed. Since that time there has been a wonderful development of this manufacture; numerous mechanical improvements having been introduced, and important chemical discoveries made.

Before proceeding with a description of the printing process it will be necessary to give some idea of the composition of the mordants employed. Of course the required intensity of shade is obtained by varying the quantity of mordant.

For purples and lilacs an impure acetate of iron is employed, which is prepared by allowing iron to oxidise or rust, and then dissolving it in the tarry acetic or pyroligneous acid obtained in the destructive distillation of wood.

For reds and pinks a sulpho-acetate of alumina is employed, prepared by mixing together impure acetate of lime and sulphate of alumina. If sufficient acetate of lime were employed, the result would be that sulphate of lime

and acetate of alumina would be produced; but the proportions taken are such that only two-thirds of the sulphuric acid combined with the alumina are replaced by acetic acid; for experience has shown that better results are obtained with this compound than with a pure acetate of alumina. This mordant may be prepared by mixing together solutions of one hundred and ninety-six parts of sulphate of alumina and one hundred and thirty-six parts of acetate of lime. In practice it is necessary to increase the quantity of acetate on account of its being more impure than the alumina salt.

For chocolate various proportions of red and black mordants are mixed together, according to the shades required.

The mordants are thickened with potato starch which has been heated to  $480^{\circ}$  F.; this renders it soluble, converting it into dextrin, a substance somewhat similar in properties to gum arabic.

The following recipes will give some idea of the proportions taken:—

*For light purple.*

- 1 gallon of acetate of iron at  $1\frac{1}{2}^{\circ}$  T.
- 3 gallons of purple assistant liquor.
- 3 gallons of water.
- 18 lbs. roasted farina.

This solution is ready for use after straining.

*For dark purple.*

- 7 gallons acetate of iron at  $2\frac{1}{2}^{\circ}$  T.
- $\frac{3}{4}$  „ purple assistant liquor.
- 3 lbs. flour.

This mixture is first boiled and then strained, after which it is ready for use.

*The purple assistant liquor* is made as follows:—

- 1st. 100 gallons wood acid.

9 lbs. yellow prussiate of potash are dissolved in the wood acid.

2 gallons sulphate of lead precipitate, made by dissolving acetate of lead in water, precipitating with sulphuric acid and allowing the sulphate of lead to subside.

2nd. 50 lbs. carbonate of soda dissolved in 8 gallons of water, to which is added 50 lbs. arsenious acid; when this is dissolved it is added to the first mixture, and thoroughly incorporated by stirring.

To the above complete mixture, add 3 gallons of hydrochloric acid and 200 lbs. of common salt. Mix well and store for use.



#### MADDER PURPLE.

##### *For light red.*

1 gallon acetate of alumina at 3° T.

1 gill bark liquor ..... at 12° T.

1 gill acetic acid.

3½ lbs. British gum.

Boil and strain.

##### *For dark red.*

1 gallon acetate of alumina at 12° T.

1 gill sapan liquor ..... at 12° T.

1½ lbs. flour.

Boil and strain.





## MADDER PINK AND RED.\*

*For light chocolate.*

2 gallons acetate of alumina at 9° T.  
 1 gill acetate of iron ..... at 24° T.  
 ½ pint logwood liquor ..... at 12° T.  
 5 lbs. of flour.

Boil and strain.

*For dark chocolate.*

2 gallons acetate of alumina at 9° T.  
 ½ gallon acetate of iron ... at 24° T.  
 ½ pint logwood liquor ..... at 12° T.  
 5 lbs. of flour.

Boil and strain.

*For blacks.*

1 gallon acetate of iron at 24° T.  
 ½ gallon wood spirit.  
 2 ½ gallons water.  
 1 pint logwood liquor at 12° T.  
 7 lbs. flour.

Boil and strain.

---

\* For the samples of madder purple and red we are indebted to the kindness of Messrs. Symonds, Cunliffe, and Co., of Manchester.

To apply these mordants they are placed in troughs in which a copper roller dips, having engraved upon it the design or pattern to be printed. The excess of mordant is removed as it leaves the solution by means of a sharp blade of steel, gun metal, or German silver, called a doctor, leaving the mordant on the engraved parts only. As the roller revolves, the calico to be printed is pressed against it by another roller, and the mordant is thus transferred to the cloth. The accompanying engraving represents the kind of machine used.

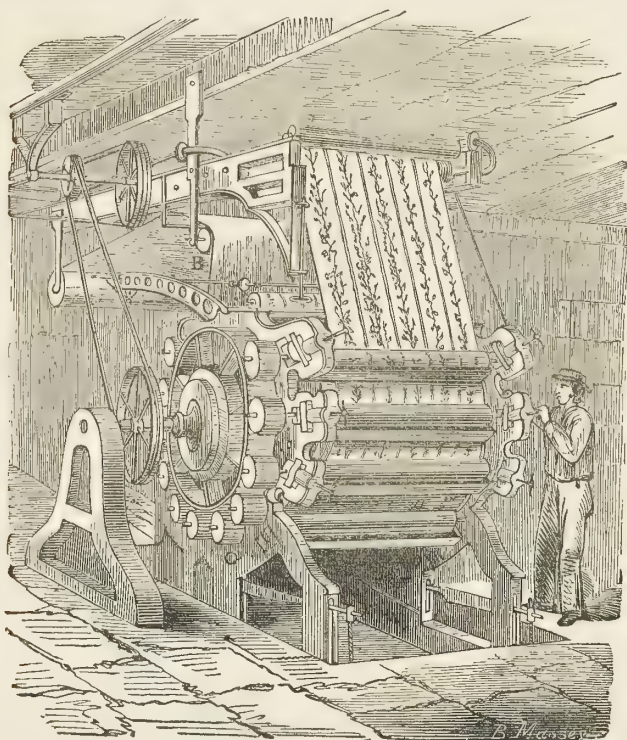


FIG. I.

By an ingenious arrangement several rollers can be mounted in the machine (as many as twenty have been used), so that a piece may receive successively mordants for different colours and of various strengths, which afterwards produce the various tints and shades which the



printer may require. The accompanying sample due to the courtesy of Messrs. Walter Crum and Co., of Manchester, will serve to illustrate the effect.



EFFECT PRODUCED BY A SIX-COLOUR MACHINE.

After this the pieces are passed over steam cylinders to dry the mordant in the calico, and are subjected to a process of ageing or fixing the mordant in the fibre. This was formerly effected by spreading out the pieces, and hanging them in a room for three or four days; the acetate of alumina thus lost part of its acetic acid, and the iron mordant nearly the whole. Some few years ago, Mr. John Thom devised a method by which this could be effected in twenty minutes; the process consists in passing the mordanted cloth over rollers fixed in a machine placed in a chamber about 20 feet long, into which a current of air and steam is thrown. The temperature must not be below  $100^{\circ}$  F. nor above  $108^{\circ}$  F., and the quantity of steam present must be such that fifty yards of calico will take up one ounce of moisture during the twenty minutes which it requires to pass it through the chamber. The printer is able to test the state of the chamber by means of wet and dry bulb thermometers,



The next operation, called dunging, received this name because formerly a mixture of cow dung and water was used in the process. Now, however, the calico is generally passed through a weak bath of alkaline silicate or arseniate of soda, mixed with a little chlorate of potash, contained in a trough in which are fixed thirty or forty rollers in two rows, one *a, b*, Fig. 2, at the top and the other *c, d*, at the bottom. The cloth is slowly passed over the rollers from top to bottom, alternately, the temperature being maintained at about 140° F.

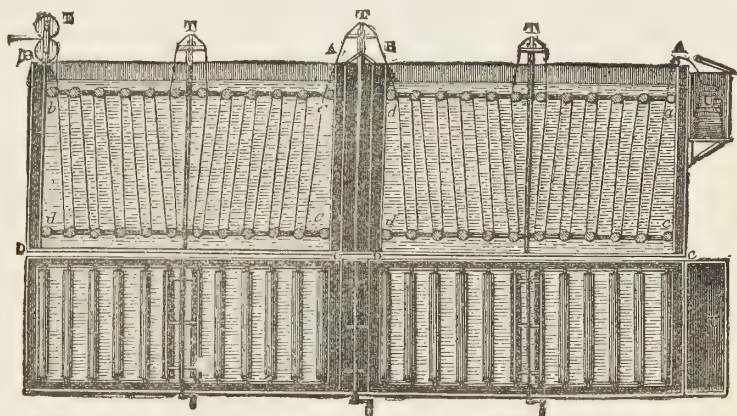


FIG. 2.

The objects of this process are, first, to effect the complete decomposition of the aluminous and iron subsalts, which are formed by removing the acid which the dessication has not expelled; secondly, to dissolve and take away from the stuff the greater part of the substances which have been used to thicken the mordant; and, thirdly, to separate from the stuff those parts of the mordant which are not combined with it, which would otherwise spread over and adhere to the unmordanted parts.

After this dunging the goods are washed and scoured in the same way as in the bleaching process, in order to remove everything which requires to be detached from the fabric.



## MADDER STYLE, MORDANTED CLOTH.

The mordanted pieces being now ready for the dyebeck, five or six of them are placed on the reel for each of the five or six compartments into which a dyebeck is divided, so that from twenty-five to thirty-six pieces are dyed in one operation.

The dyebeck is constructed as follows:—

A, Figs. 3 and 4, is a wooden or iron trough, about 6 feet in length, 4 feet in width, and 4 or 5 feet in depth, into which the madder and water required for a dyeing are introduced. This vessel is surmounted with a wince or wheel B, and divided in the direction of its length by four partitions *b, b, b, b*, and thus presents five distinct compartments, into which the goods fall on quitting the reel B. This reel, containing six or eight wooden spars on its circumference, is furnished at one end of its axis with pullies put in motion by means of a strap driven by any moving power; it is always moved by the hand in dyeing fine fabrics, such as muslins, balzarines, &c. C, C, C, C, are wooden panels or lids with hinges, to be opened and shut at pleasure. The upper two open from below or upward, the lower two from above and downward. D, E, are hollow copper rollers, under which



the goods pass on quitting the compartments *b, b, b, b*. *f* is a tube pierced with a multitude of holes, through which the steam is introduced at pleasure by the tube *h* communicating with a generator. A screw valve affords the means of regulating the introduction of the steam into the tube *f*. There is also a pipe in connection with a reservoir of water, through which, by means of the stop-cock *g, k*, the quantity of water required for the operation can be introduced into the trough *A*.

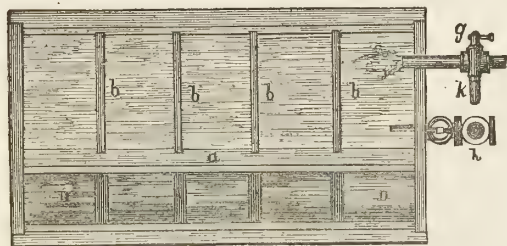


FIG. 3.

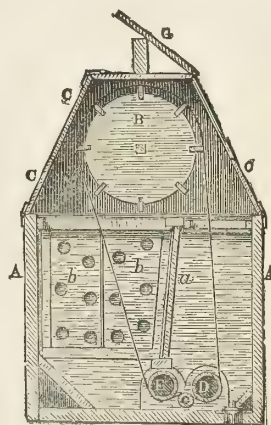


FIG. 4.

The working of the apparatus is very simple; into each compartment are put the requisite number of pieces; after passing the pieces over the wince and under the rollers *D, E*, they are fastened together by the ends so as to form as many endless webs as there are compartments. The pullies are then set in motion, and the shaft of the reel being in connection with them draws the goods in such a manner that, passing out from under the cylinder *D*, they rise, pass over the reel to fall back into the compartment *b*, slide over the inclined plane, arrive again under the rollers *D, E*, and so on during the whole operation.

The object of the compartments is to prevent the pieces getting too much intermingled, as they would then cease to obey the circulating movement and take the dye unequally.



The pieces are first introduced into the vats with cold water, and from 5 to 7 lbs. of madder or ground Turkey roots per piece; the temperature is then gradually raised in the course of an hour and a half to 180° F.

From the results of Schunck's experiments it would appear that the effect of this is to give as much time as is practically possible for the xanthin of Kuhlmann to unfold into rubian and chlorogenin, and to allow the erythrozym of the madder to decompose the glucoside or glucosides of the madder into sugar, and alizarin or purpurin. If the temperature were raised too rapidly the erythrozym would become coagulated before it had time to effect the complete decomposition of the glucosides.

The chlorogenin, pectic acid, rubiacin, verantin, rubiretin, &c., act very injuriously on the colours produced from the madder, making them dull and weak and the whites dirty. To obviate this a certain quantity of chalk is added to the bath. The action of the lime appears to be that it forms insoluble combinations with these injurious colouring principles, and leaves the alizarin to combine with the mordants. With Avignon madder, this addition of chalk is unnecessary, for being grown on a calcareous soil, it generally contains sufficient lime naturally, whilst, on the contrary, it must always be used with Turkey roots and Alsace madder.

That the action of the lime is as above stated, is shown by the fact that when a proper proportion of chalk is added the colours are not only brighter but are also more permanent, whilst if an excess of chalk is employed the strength and beauty of the colours are injured. The fact was observed many years ago by Robiquet, and has recently been confirmed by Schunck, that when a small amount of lime is added to alizarin it proves injurious to the intensity of shade produced by a given quantity of alizarin; and Schunck proved also that the addition of rubiacin, or

any of the other resinous colouring matters, to alizarin during the dyeing process produces very prejudicial effects. They weaken the colours and render them impure and unsightly; the red acquires an orange, and the purple a reddish hue, whilst the blacks become brownish, and the white parts assume a yellow tinge. These effects entirely disappear as soon as the foreign colouring matters are completely saturated with lime. On the contrary, Rosenstiehl\* states that perfectly pure alizarin, with distilled water, dyes but very imperfectly; and that, in order to obtain satisfactory results, it is absolutely necessary that a certain quantity of carbonate of lime should be present.

In the preceding chapter it was stated that erythrozym was a compound containing lime, and that if this lime were once removed the erythrozym became inactive and permanently altered; it is important, therefore, that lime should be added, to prevent the free acids acting injuriously on this compound.

Having thus briefly noticed the changes which take place in the hour and a half during which the temperature is gradually raised, we will return to the description of the dyeing process. Full steam is now turned into the beck so as to heat the liquor as near  $212^{\circ}$  F. as practicable. The effect of this, as shown by the table of solubility of alizarin already given, is to increase the amount of alizarin in solution, and thereby facilitate its combination with the mordant. When the dyeing is completed the pieces are removed from the beck, and thoroughly washed in a washing machine.

---

\* Compt. Rend., lxxix., 680.





MADDER STYLE AFTER DYEING.

The fifth operation is the soaping, to remove the excess of colour and clear the whites; the becks used being similar to those employed for dyeing. A sufficient amount of soap of good quality is dissolved to produce a perceptible froth, and the goods, arranged as for dyeing, are kept constantly revolving on the reel. The temperature of the beck is maintained at 180° F. They are then taken out, thoroughly washed, and subjected to a second soaping. After another thorough washing, the pieces are passed through a slightly alkaline hypochlorite of soda solution, to which is added a little sulphate of zinc.



MADDER STYLE CLEARED.\*

\* Messrs. Symonds, Cunliffe, and Co., of Manchester, have kindly furnished the three specimens of madder style.



Some twenty years ago, whilst professionally engaged in a printworks, the author made a series of experiments with a view of decreasing the serious expense involved in employing such large quantities of soap in the above operations, and found that madder goods could be steeped even for days without injury in a *decidedly alkaline* solution of hypochlorite of soda, prepared by making a neutral hypochlorite of soda, and adding an ounce of crystallised carbonate of soda per gallon, and that by employing this solution such a quantity of the chlorogenin and resinous compounds already described were removed, that one soap-ing operation could be dispensed with.

The difficulty and expense experienced by calico printers in brightening their colours and obtaining pure whites in madder-dyed goods, attracted many years ago the attention of scientific and practical men, and any process by which these difficulties might be overcome was anxiously looked for. The discovery by Robiquet and Colin, that the colour-giving principle was not destroyed by sulphuric acid, was the first step in that direction, and led Schwartz to observe that the carbonaceous mass of Robiquet might, if carefully washed and neutralised, be used as a dyestuff. Messrs. Lagier and Thomas improved upon this, and in 1839 introduced an article which is now extensively used by calico printers under the name of garancin. It is generally prepared in the following manner: Madder is treated with eight or ten times its weight of water and allowed to stand for twelve hours. This liquor is then run off and reserved for treatment in a manner similar to that obtained in the manufacture of *fleurs de garance* which will be described further on. The washed madder is introduced into large wooden vats lined with lead, and a quantity of water added sufficient to make the whole into the state of a thin paste. 35 lbs. of sulphuric acid are now added for every 100 lbs. of

madder originally taken. The vat is then closed and the madder steamed for several hours,\* after which it is mixed with a large quantity of cold water and run off into a vat with a false bottom of woollen, where it is washed methodically with water until the latter takes a slightly pink hue; this is an indication that all the acid has been removed. Some manufacturers to save time add a small quantity of carbonate of soda to the last washing liquor, and Messrs. Dollfus, Mieg, and Co. have suggested the employment of ammoniacal vapours to effect the same purpose. The garancin is placed on trays in a chamber where it is submitted to the action of the ammonia. They state that their 'garancine modifiée' gives much richer and brighter colours, and that the purples are especially improved. When the garancin has been thoroughly washed, it is placed in centrifugal machines to drive off the water as far as possible and is then submitted to hydraulic pressure. The pressed cakes thus obtained are put in drying stoves, and when quite dry are ground with mill-stones and sieved.

The attention of the French government having been called to the pollution of the rivers which receive the washing liquors of the garancin manufacturers in the neighbourhood of Avignon, they were called upon to devise some method of abating this nuisance, as it had increased to such a degree as to endanger the health of the inhabitants, and to cause great injury to the land-owners.

M. Pernod, one of the largest manufacturers of garancin and *fleurs de garance* in the department of Vaucluse, gave the subject his attention, and contrived a process by which he not only removed nearly the whole of the organic matter in suspension and neutralised the acid, but even

---

\* Stenhouse has observed that a large quantity of a compound called furfural is produced during this operation.



effected a saving, for he discovered that the spent liquor of garancin contains a large quantity of oxalic acid. In his process the whole of the spent liquor of a day's working is run into a large reservoir, and slacked lime is added to it in slight excess. After two or three hours, the clear liquor which may now be considered unobjectionable, is run off into the river. The lime deposit after being pumped up into smaller reservoirs and mixed with a slight excess of dilute sulphuric acid is allowed to stand for twelve hours, when the liquor is run off and the precipitate thrown on a woollen filter. This precipitate, which consists of sulphate and oxalate of lime mixed with a small quantity of colouring matter, is boiled in a leaden vessel with an excess of sulphuric acid; this decomposes the oxalate of lime, sulphate of lime is formed, and the liberated oxalic acid dissolves in the acid liquor. It is filtered through flannel whilst hot, and on cooling deposits a large quantity of oxalic acid in the crystalline state.

One hundred parts of madder yield from thirty-four to thirty-seven of garancin, according to the variety of madder used. Turkey roots are usually employed to prepare first-class garancins for purples and lilacs, French madders and Naples roots for pinks and reds, and Dutch madders for dark reds and chocolates. Twenty million pounds weight of madder are annually employed in the neighbourhood of Avignon for the manufacture of garancin.

The dyeing power of a good garancin is from four to five times as great as that of the madder from which it is made. The gain, therefore, apart from the greater purity of colour in the garancin, is from 70 to 85 per cent. on the original madder. This increased dyeing power is due to the complete decomposition of the rubian and other glucosides the root may contain, and possibly also to the liberation of a certain quantity of colour-giving principles which may be combined with the lime and magnesia present.



For garancin style only  $1\frac{1}{2}$  to 3 lbs. of garancin are employed per piece. The dyeing operation is conducted in a manner very similar to that of madder styles, except that the temperature of the beck never exceeds  $180^{\circ}$  F.

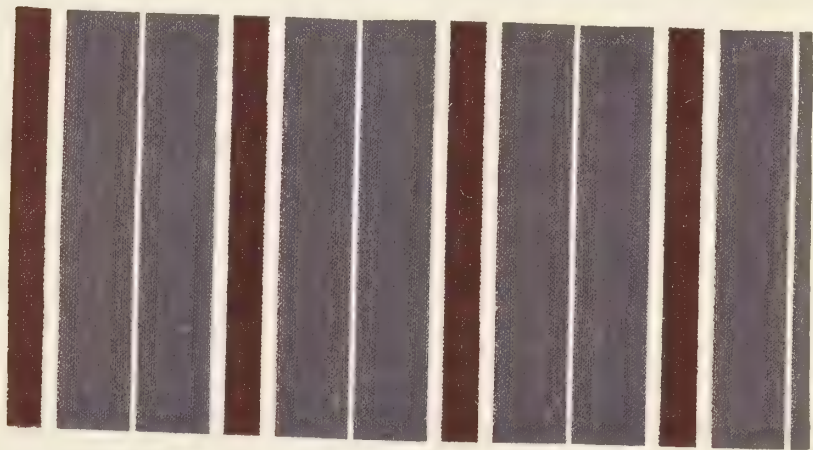
The advantages of garancin over madder are, that the goods dyed with it require only a slight soaping and passing through a clearing liquor of very weak alkaline hypochlorite of soda and a little sulphate of zinc, for the goods to be ready for the stiffening and calendering processes. On the other hand the colours are not so fast, for they will not resist the action either of light or of soap to the same degree as madder-dyed goods. Moreover, the colours, except the purples, are far less brilliant; and, although the addition of a little chalk to the bath in the dyeing process tends, by neutralising the traces of acid which commercial garancin usually contains, to improve the colours obtained, yet there is still a marked inferiority to madder. The following illustration of the garancin style has been kindly furnished by Messrs. Wood and Wright, of Manchester.



GARANCIN STYLE.

In 1852, Messrs. Schunck and Pincoffs effected an improvement in the manufacture of garancin, their product

being known in England under the name of 'commercial alizarin'; but on the continent it is better known as 'pincoffin.' Their process consists in submitting ordinary garancin to the action of high-pressure steam of a temperature of 300° F., which, whilst it does not act on the alizarin contained in the garancin, destroys the rubi-retin and verantin. The employment of commercial alizarin is especially advantageous in the production of purples, which are faster and more brilliant than those produced by ordinary garancin. The cloth also does not require soaping or clearing.



DYED WITH 'COMMERCIAL ALIZARIN.'

We are indebted to the kindness of Mr. S. Pincoffs for this sample dyed with 'commercial alizarin.'

In 1843, M. Leonard Schwartz, of Mulhouse, patented the right of treating spent madder from dyebecks by the same process as that employed for the conversion of madder into garancin. To the product so obtained he gave the name of *garanceux*. At the present day this process is carried out by every large madder dyer.

Messrs. Julian and Roquet have devised a process for preparing a purified madder which they call *fleurs de*



*garance*, or flowers of madder, of which many million pounds per annum are now manufactured in France. It not only yields brighter colours than the original madder, but as it does not soil the white parts of prints, its use saves the printer much soap and labour. It possesses also another great advantage. The printer can obtain the same intensity of shade by employing mordants about fifteen times weaker than when madder in its original state is employed. This is owing to the *fleurs de garance* no longer containing any soluble matters, especially acids like pectic acid, &c., which during the process of dyeing dissolve and remove such a large proportion of the mordant.

To prepare the *fleurs de garance*, madder is mixed with eight or ten times its bulk of water and allowed to stand for twelve to fifteen hours. When Avignon madders are used and the *fleurs* are intended for the production of reds or pinks, one part of sulphuric acid for every hundred of roots is added to the water to neutralise the carbonate of lime which that madder always contains. This addition of acid is unnecessary when Alsace and Dutch madders are used, or when the *fleurs* are intended for the production of purples or chocolates. When the maceration is finished the liquor is run off into proper vessels to be fermented, so as to transform the sugar into alcohol. The solid matter is placed in bags, submitted to hydraulic pressure, and after being dried in stoves and ground, is ready for use. A hundred parts of madder yield fifty-five to sixty of *fleurs de garance*. It may be stated *en passant*, that the injury which Dutch and Alsace madders sustain when kept too long in casks, is doubtless owing to the fact that after the erythrozymic fermentation is completed, an alcoholic and lactic one sets in, which acts injuriously on the colour-giving principles.

The alcohol prepared by the fermentation and distilla-



tion of the liquids obtained in the above process has a very disagreeable taste and odour, and is only fit for manufacturing varnishes and ether, and for other commercial operations. This seems to be caused, to some extent at least, by the presence of acetic ether and aldehyde, in fact the latter substance may be easily obtained from madder alcohol by careful rectification. At Sorgues, near Avignon, there is a large distillery where the greater part of the alcohol produced in the manufacture of *fleurs de garance* and garancin is rectified. The method employed appears to consist in passing the alcohol vapours through wood charcoal.

Various extracts of madder are prepared on a large scale, all of which contain alizarin or purpurin in a more or less pure form. They are applied in a different manner to those preparations hitherto noticed, being printed on along with the mordant, and then dried and submitted to dry high-pressure steam for one or two hours, when the colours become fixed on the fabric.

Calico printers have long desired to obtain these extracts, and although many chemists and printers have worked on the subject, among whom may be mentioned Persoz, Claubry, Fauquet, Girardin, Gerber, Dollfus, Verdeil, Michel, and Schützenberger, yet they have failed in introducing this class of product into the trade. This result is no doubt generally to be attributed to their impurity, although several extracts, especially those of Messrs. Fauquet and Girardin and M. A. Hertmann have been employed. Their use, however, was confined to single firms, and in these only to a limited extent.

The house of Messrs. Scheurer, Roth, et Fils, of Than, were the first to successfully apply these extracts; the products employed being Kopp's purpurin and green alizarin, prepared by Messrs. Schaaff and Lauth, of Strasbourg. M. Leitenberger also used an extract manufactured by M.

Brosch, of Prague, who followed a process discovered by Rochleder, but which is kept secret. M. Pernod's extract was also soon after in use, and the splendid specimens exhibited at the Paris Exhibition in 1867 by the two firms above mentioned, and several other Alsace houses, could leave no doubt of the success of these products.

The printing of the colour-giving principles of madder on fabrics must be considered as the greatest improvement in calico printing since the introduction of coal tar colours, and there can be scarcely any doubt but that it will in time completely revolutionise the trade.

If we compare the length of time, the amount of trouble, and the numerous processes required to produce by the ordinary method a piece of printed madder goods—the printing of the mordant, the ageing, the dunging, the dyeing, once or twice soaping and clearing, and the thorough washing between each of the last four operations—with the simple process of printing the colour, steaming, washing, and soaping, the truth of this statement will at once be evident.

The process of M. Leitenberger, is based on the fact that purpurin is soluble in water at 130° F., whilst alizarin only dissolves at 170° F. He mixes madder with water and heats the whole gradually by means of a jet of steam to 130° F., at which temperature it is maintained for some time. The liquor is then run off and filtered, and the operation is repeated until the madder ceases to yield any soluble matters. To the clear solution, lime, or still better, baryta is added, when a lake precipitates, which is collected, washed, and mixed with hydrochloric acid. The purpurin thus liberated is thrown on a filter and washed, when it is ready for use. The madder remaining from the above operation is dried and heated with wood spirit in closed vessels to extract the alizarin. The operation is repeated until no more alizarin is dissolved. This extract is slowly

poured into water, care being taken to agitate well ; a hydrate of alizarin is thus precipitated, which, according to M. Leitenberger, is less soluble than alizarin itself. This when collected and washed is ready for use.

Another process is that patented by Mr. Paraf, in December, 1868. He avails himself of the extraordinary increased solubility of alizarin in water at high temperatures, mentioned in the preceding chapter. He has devised an apparatus by which he is able to treat madder with water under a pressure of four or five atmospheres, and when the liquor is saturated to draw it off from the solid matter remaining in the apparatus. As the aqueous liquor cools, the alizarin separates in the form of flocks, which, when collected and washed, are ready for use as an extract. He finds that the solubility is increased by adding a small quantity of alum or sulphuric acid to the water employed in the operation.

A third process, that of M. Emile Kopp, is based on Schunck's discovery that weak acids act in a similar manner to erythrozym in causing the rubian to split up into sugar and alizarin. Kopp observed, some years ago, that a solution of sulphurous acid dissolved the glucosides of purpurin and alizarin without change; and he has since applied this observation to the development of the following elegant process for the preparation of alizarin and purpurin:— 600 lbs. of Alsace madder are macerated for twelve or fifteen hours, with 800 gallons of a weak solution of sulphurous acid, to which is added one-thousandth part of hydrochloric acid to neutralise the earthy carbonates existing in the root. This operation is repeated three times. To the liquors 3 per cent. of sulphuric acid is added, and the whole heated to a temperature not exceeding 140° F., when red-coloured flakes separate and gradually deposit ; these when washed and dried are commercial purpurin. The clear liquor after being boiled for



a couple of hours and allowed to cool, deposits a dark green powder, which when washed and dried is known as 'green alizarin.'

Kopp has still further improved upon this process, which he devised in 1856, and instead of obtaining commercial purpurin and green alizarin he is able to produce an alizarin which he calls alizaric extract, so pure that it can be used for printing purples and lilacs, and a second which is used for printing reds, pinks, and chocolates. By employing methodic lixiviation and modifying his mode of operation, he has also been able to save the saccharine matter existing in the madder and to convert it into alcohol.

To prepare the alizaric extract for purples and lilacs, one part of green alizarin is boiled with fifteen or twenty parts of petroleum oil, having a boiling point not exceeding 300° F., which dissolves the alizarin and leaves the green matter, probably chlorogenin. After a quarter of an hour's ebullition it is left to stand for a few minutes, in order to allow the green matter to settle, which it does rapidly. The clear liquor is then poured off and allowed to cool to 212° F., when a certain quantity of nearly pure alizarin is deposited in the form of small yellow crystals. The supernatant liquid is mixed with 10 or 15 per cent. of an aqueous solution of caustic soda, containing 5 to 8 per cent. of soda, and the whole strongly agitated. The alkaline solution takes out the whole of the alizarin, and when decanted and rendered slightly acid with dilute sulphuric acid deposits the colouring matter as a crystalline mass. This is fit for use as soon as it has been collected and washed; it is sold under the name of yellow alizarin.

To prepare the extract for pinks and reds, the madder which has been exhausted by sulphurous acid to obtain purpurin and green alizarin, is introduced into bags and subjected to hydraulic pressure. It is then placed in vats

and lixiviated with a weak solution of caustic soda ash (1 to 1½ per cent.); being gradually heated to boiling. The alkaline liquor which contains the colouring matter, pectic acid, fatty matters, resins, &c., is removed into large vats, and is there mixed with the acid liquors from which the purpurin and green alizarin have been separated, in such a proportion that the liquor has a distinctly acid reaction. An abundant gelatinous precipitate is thus produced, which, when collected, washed, and dried, is called pectic extract, and can be employed for dyeing purposes. To prepare an extract sufficiently pure for printing, the gelatinous precipitate is mixed with an acid solution of sulphate of alumina, marking 4° to 6° Baumé, and containing 4 to 6 per cent. of free acid. The mixture is then boiled for fifteen or twenty minutes and filtered rapidly. As the filtered liquor cools orange flakes are deposited, which are collected and mixed with ten or fifteen times their volume of water, containing from 5 to 8 per cent. of sulphuric acid. The whole is kept at a temperature of 195° F. for an hour, allowed to cool, and the mass thrown on a filter and washed first with acidulated water and then with pure water. There remains a beautiful orange magma sold under the name of orange extract of madder. It is employed for printing chocolates as well as reds and pinks.\*

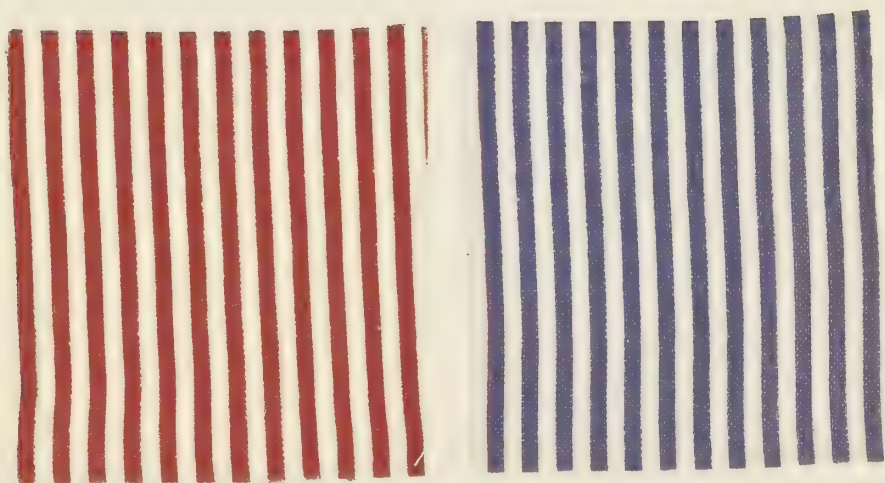
This manufacture has been carried on by Messrs. Schaaff and Lauth for several years, and doubtless yields a larger amount of colour-giving principle than M. Leitenberger's method, for the glucosides must be more completely decomposed in these processes than by water alone.

The dyeing power of alizarin thus obtained is equal to forty times its weight of madder, and ten times its weight of garancin.

---

\* For full details and the description of the preparation of alcohol from the residue, see Bulletin Société Industrielle de Mulhouse, xxxvii., 437.

It is to the kindness of Messrs. Dollfus, Mieg, and Co. that the author is indebted for the accompanying beautiful specimens of these colours, which have been obtained with the products manufactured with so much skill by Messrs. Schaaff and Lauth.



Another extract is that manufactured and patented by M. Pernod. It is largely used at the present time in Lancashire as a topical colour.\* His process consists in exhausting garancin by methodical lixiviations with boiling water, containing five parts per thousand of sulphuric acid. As the acid liquor cools an orange-red precipitate falls to the bottom of the vat, which is collected and washed until entirely free from acid: this is readily ascertained, as the washing water assumes a pinkish hue immediately the last trace of acid is removed. The

---

\* This term is applied to a colour which is printed on a fabric and afterwards fixed by the action of steam.



extract so obtained is exhausted by boiling alcohol in a properly constructed apparatus, in order to dissolve out the colouring matter. The alcoholic extract is mixed with one quarter its bulk of water, introduced into a retort, and the alcohol recovered by distillation. The residue remaining in the retort is thrown on a filter and washed with water, when it is ready for use.

The last process which it is necessary to notice, although perhaps not so practicable as those previously given, is yet interesting in itself, being probably the first case in which bisulphide of carbon was employed for extracting colours. According to this method, which was patented by M. Alfred Rien, in February, 1870, dry *fleurs de garance*, or garancin, are placed in suitable closed vessels with heated bisulphide of carbon. The liquor is run off whilst hot, and the sulphide of carbon is removed by distillation. The residue left in the retort is dissolved in weak alkali, and the colouring matters precipitated by the addition of sulphuric acid in quantity sufficient to exactly neutralise the soda. The flocculent precipitate of alizarin and purpurin after being washed is ready for use.

The following recipes may prove useful, as they show the proportions necessary to produce the various shades.

*For dark reds.*

Take 8 lbs. of extract of madder,  
4 lbs. of acetic acid, and  
1  $\frac{1}{4}$  lbs. of starch.

Boil these in an earthenware vessel, and when cold add to six measures of the above one of acetate of alumina, and a very small quantity of Gallipoli oil—say one per cent.

*For a pink.*

Take 4 lbs. of extract of madder.  
2 lbs. of acetic acid.  
10 quarts of gum Senegal water.  
1 pint of acetate of alumina.

*For a purple.*

Take 1 pint of extract of madder.

½ pint of acetic acid.

½ pint of water.

3 oz. starch.

Boil, and when the mixture is cool add 5 oz. measure of acetate of iron at 24° T., and 5 oz. water.

For a chocolate proceed as in the last recipe, substituting acetate of chromium for acetate of iron.

*For a red.*

Boil together 2 litres of (Pernod's) extract in paste.

1½ litres of acetic acid at 8° Baumé.

448 grammes of olive oil.

After boiling, the acid which has evaporated is replaced, and the mixture is thickened with 1,500 grammes of gum Senegal in powder.

When the colour is required for use, to the above mixture is added ½ a litre of acetate of alumina at 15° Baumé. It is important to add the mordant with care and just before use, otherwise the combination of the mordant with the colouring matter takes place before the printing, and there is considerable loss of the latter.

*For dark purple.*

Boil together 1 litre of extract (Pernod's) in paste.

1 litre of acetic acid at 8° Baumé.

224 grammes of olive oil.

The acid which is evaporated is replaced, and the mixture is thickened with 600 grammes of powdered gum Senegal. When required for use there is added

224 grammes of black mordant at 10° Baumé.

128 grammes arsenite of soda at 6° Baumé.

A second is,

Take 9 litres extract (Pernod.)

8 litres acetic acid at 8° Baumé.

20 litres gum water of 1,000 grammes of  
gum per litre of water.

2 litres black mordant at 10° Baumé.

If the dry extract of Rochleder be employed, the quantity must be calculated on the basis of five parts of Pernod's being equal to one of Rochleder's.

After the cloth is printed the pieces are hung to dry for a certain time, then submitted to the action of dry high-pressure steam for an hour and a half or two hours.

Schützenberger states that pure alizarin gives very beautiful purples, but the reds have a violet shade. The best reds he considers are obtained with extracts containing both purpurin and alizarin, and a certain proportion of yellow colouring matter. On the other hand, these extracts give only dull purples.

Up to the time of the introduction of printing the extracts, chocolates were obtained with madder by means of a mixture of iron and alumina salts. It was, however, found difficult to produce fine shades by this mixture in printing, and Mr. Horace Kœchlin made a series of experiments to ascertain whether any of the other metallic oxides could be employed with the extract of madder to produce some new and useful shades. He prepared acetates of twenty-two metals, and made a mixture of each with Pernod's extract thickened with gum. After printing these mixtures on the fabric and steaming it for two hours, he obtained the following results:—

|          |                 |
|----------|-----------------|
| Silver   | Rose.           |
| Antimony | Yellowish rose. |
| Bismuth  | Bright rose     |
| Barium   | Dirty shade.    |
| Calcium  | Bright rose.    |
| Cadmium  | Bright rose.    |
| Copper   | Bright rose.    |
| Chromium | Chocolate.      |
| Cobalt   | Bright rose.    |
| Tin      | Red.            |
| Glucinum | Red.            |

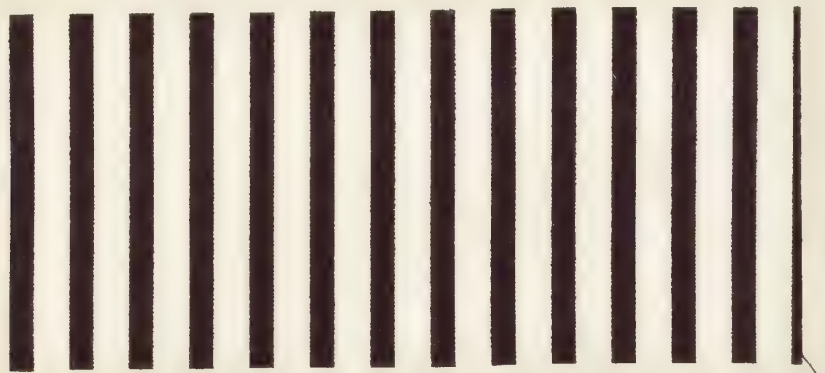


|                   |                           |
|-------------------|---------------------------|
| Magnesium         | Bright rose.              |
| Mercury           | Bright rose.              |
| Manganese         | Bright rose.              |
| Molybdenum        | Bright rose.              |
| Gold              | Bright rose.              |
| Platinum          | Grey violet.              |
| Palladium         | Olive shade of the oxide. |
| Lead              | Rose yellow.              |
| Tungstate of Soda | Rose yellow.              |
| Uranium           | Grey or drab.             |
| Zinc              | Rose.                     |

From these results he concluded that the only two metallic oxides which could be used with marked advantage in connexion with these were the oxides of uranium and chromium, the former for greys and the latter for chocolates. Acetate of chromium is now used in the trade for the production of chocolates, and the following is the recipe given by M. Spirk :—

Take 2 litres (Pernod's) extract in paste.  
 2 litres acetic acid at 7° Baumé.  
 3 litres acetate of chromium at 17° Baumé.

For the following sample, which represents the effect obtained with chromium acetate, we are indebted to the kindness of M. K. Koechlin, of Alsace.



CHROMIUM MORDANT.

To obtain the uranium grey the following proportions are employed :—

- 2 litres extract of madder in paste.
- 2 litres acetic acid at 7° Baumé.
- 3 litres acetate of uranium at 10° Baumé.

#### URANIUM GREY. (K. KOEHLIN.)

The following recipes are used with success in printing with artificial alizarin. It is delivered in two forms, pure or in paste containing 10 per cent. The recipes are for the latter.

##### *For a red.*

- Take 2,500 grammes alizarin.
- 8,000 grammes thickening.
- 500 grammes acetate of alumina at 10° Baumé.
- 250 grammes chalk at 16° Baumé.

The red is obtained by adding one part of this mixture to two parts of thickening, then printing and steaming. It is afterwards passed through a bath heated to 120° or 140° F., and composed of 1,000 litres of water, 30 kilos. of chalk, and  $1\frac{1}{2}$  kilos. of chloride of tin, or 20 kilos. of chalk and 5 kilos. of arseniate of soda ; it is then brightened.

The thickening is made of 6 kilos. of starch, 20 litres of water,  $\frac{1}{4}$  litre of acetic acid, 10 litres of gum tragacanth (2 ounces of gum per litre), and of 1.5 kilos. of olive oil.

The following is another recipe :—

- 4 or 5 kilos alizarin.
- 10 litres thickening.
- 300 to 400 grammes nitrate of alumina at 15° Baumé.  
(prepared from nitrate of lead and alum).
- 600 grammes acetate of alumina at 10° Baumé.
- 400 to 500 grammes acetate of lime at 16° Baumé.

The use of nitrate of alumina gives a red of a more orange shade than is obtained with the acetate.

*To produce purple.*

Take 1,400 grammes alizarin.

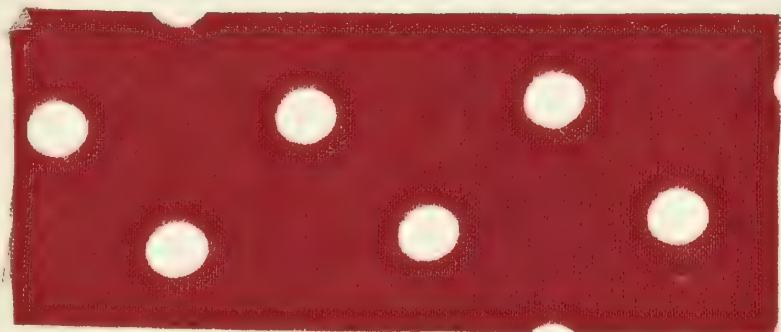
10 litres thickening.

200 grammes black mordant at 12° Baumé.

370 grammes acetate of lime at 16° Baumé.

The thickening is formed of 5 kilos. starch, 18 litres water, 9 litres gum tragacanth, 3 litres acetic acid at 6° B., and 1 kilo. of olive oil.

The printed fabrics are steamed under a pressure of half an atmosphere for twenty-four hours. They are then passed for two hours in a bath of arseniate of soda (5 kilos. arseniate, 20 kilos. chalk, and 1,000 water) at 120° to 140° F., washed and brightened in a bath of soap (3 kilos. of soap to twenty pieces of fifty yards).



TOPICAL STYLE WITH ARTIFICIAL ALIZARIN.

One of the most serious objections to the use of madder as a topical colour, has been the small amount of colour fixed, compared with the quantity used, and consequently the great loss which occurs in the washing, after steaming. We are therefore much indebted to Messrs. Scheurer, Roth, et Fils, of Alsace, for publishing the following simple process for its recovery :—

The pieces are washed in a beck containing chalk or



gelatinous alumina, which takes up the colour as it comes off the cloth and prevents it soiling the whites.

When the washing liquor in the beck is sufficiently charged with the colouring matter, the matters in suspension are allowed to settle, and the deposit thrown on a filter. It is then removed from the filter and mixed with weak sulphuric acid if alumina has been employed, or hydrochloric acid, if lime. The mineral matters and gum or starch are dissolved, leaving the colouring matter in an impure state. This is washed, dissolved in a weak solution of soda, filtered, and on the addition of an acid the colour-giving principles are precipitated, and after washing are ready for use.

There is another source of loss also for which M. Carlos Kœchlin has devised a remedy. The acetic acid employed in the mordants is found to act rapidly on the doctors of the printing machine when they are made of steel. The iron thus dissolved combining with the colouring matters of the extracts soon dims the brilliancy of the reds, pinks, and chocolates produced by an alumina or chrome mordant. The troughs must consequently be emptied, and the colouring principles are recovered as follows :—

For every 12 quarts of refuse printing liquor containing  $\frac{1}{2}$  lb. of Pernod's extract 4 quarts of concentrated sulphuric acid are added and the whole heated for two hours in a water bath. The insoluble matter is then well washed and is equal in every respect to the original extract.

The waste soap liquors which are produced in such large quantities in the clearing of madder-dyed and printed goods, if allowed to run into rivers not only pollute the stream, but as they contain a considerable amount of colouring matter, there is also a loss of valuable material. Messrs. Thom and Stenhouse, in July, 1872, took out a patent\* for the recovery and utilization of this soap waste

---

\* No. 2,186.

in the following manner: A solution of chloride of calcium is run into the soap liquors in a large cistern until no further precipitation takes place, and milk of lime is then added so as to render the solution decidedly alkaline; for this purpose about 43 lbs. of quicklime are required for every 20,000 gallons of the soap liquor. After thoroughly mixing and allowing it to stand for twelve hours, the clear liquor, which is almost colourless, is drawn off, and the precipitate is pumped into a smaller cistern, where it is treated with hydrochloric acid in quantity just sufficient to decompose the lime soap. The liberated fatty acids, and the colouring matter which exists as a lake, are collected on woollen filters and pressed at first cold, and then under hot water; by this means nearly all the fat is squeezed out. The pressed cake is then treated in a properly constructed apparatus with light petroleum to dissolve and remove the last traces of fat from the valuable colouring matter, which is finally boiled with dilute sulphuric acid, and washed with cold water until free from acid in a manner similar to that practised in making garancin. The colouring matter thus obtained is equal in dyeing power to three or four times its weight of the best garancin.

The preparation of madder lake, which is used in oil and miniature paintings, for colouring artificial flowers, &c., may now be briefly described. It is equally permanent with the colours fixed on fabrics, and is consequently much prized by the painter.

There have been several processes proposed for its preparation, but the two following by M. Persoz appear to be the best:—

Madder washed with water containing sulphate of soda is boiled for twenty minutes with ten times its weight of a solution of alum, containing one part of alum in ten of solution. It is filtered and allowed to cool to 90° or 100° F. The red liquor may then be treated by two

methods. By the first it is cautiously saturated with carbonate of soda, say one-eighth or a tenth, according to the amount of alum employed, by which a basic alum is formed, which remains in solution. The liquor is now boiled and an insoluble subsulphate of alumina is precipitated, which is combined with all the colour in the bath. The precipitate is not gelatinous, but separates and filters rapidly. It also dissolves easily in acetic acid. By the second method seventy-eight parts of acetate of lead for one hundred of the alum employed are added to the liquor, on which there is a precipitate of sulphate of lead. The red liquor is filtered and boiled, when the colouring matter is precipitated in combination with the insoluble basic sulphate of alumina. The lake obtained by the latter process is much purer, and the colour more intense than that obtained by the carbonate of soda process.

Instead of employing madder in the above preparations, it is more convenient to use either the extracts, or, perhaps best of all, commercial purpurin, which is at present little used in dyeing.

The last point to be considered in relation to madder and its preparations, is the determination of its comparative value.

It is easy to understand that a dyestuff so high in price as madder offers great inducement to the dishonest dealer for adulteration. For this purpose both mineral and organic substances are used, among which may be enumerated:—

*Mineral Matters.*

Powdered brick.

Ochre.

Yellow sand.

Yellow clay.

*Organic Substances.*

Oak sawdust.

Mahogany sawdust.

Various ground dyewoods.

Fustic.

It is easy to ascertain if it has been adulterated with any mineral substance, as on incineration good madder yields only from 9 to 11 per cent. of ash, and if the amount ex-



ceeds this it will indicate that it has been adulterated with some inorganic matter.

To determine the amount of extraneous matter of an organic nature is not so easy. One of the best methods is to compare the dyeing power of the suspected sample with madder of known good quality.

This is effected by placing twelve grains of each of the samples to be compared in pans of copper or block tin with a quart of water. These pans are placed in a water-bath heated by means of a jet of steam. A piece of calico mordanted with red, purple, and chocolate mordants which cover about three-fourths of the surface of the cloth is placed in each pan. It is important that each strip taken should be about three inches in breadth, and its length equal to one-half the breadth of the calico (twenty-six inches). The swatches are placed in the pans whilst cold; steam is then turned on, and, as in practice, the temperature is gradually raised during an hour and a half to 180° F., and then for half an hour kept as near the boiling point as possible. During the whole time of the operation the pieces should be constantly and carefully lifted out of the dyeing liquor, either with a glass rod, or better still by a mechanical arrangement. When the dyeing is completed, the pieces are thoroughly washed with pure water and the brilliancy and intensity of shade carefully compared. If the samples under trial are found to be weaker than the standard, the dyeing operation is repeated, adding such a quantity of the inferior madder as will bring up the colour to the same intensity as the standard. The values are in inverse ratio to the quantities taken: thus, if it requires eighteen grains of the sample under examination to give the same depth of colour as twelve grains of the standard sample, it has only two-thirds the dyeing power.

A further trial is, however, necessary to arrive at a correct conclusion as to the value. The dyed pieces are

divided into two parts, one of which is kept for a comparison, whilst the other is submitted to a light soaping; three or four grains of soap to one quart of water being sufficient for the surfaces above given. They are carefully heated in this solution for half an hour, the temperature being kept at 180° F. They are then washed and dried, and the tints again compared.

The first operation gives the total amount of colour; the second removes any colouring matter of the dyewoods, such as sapan and peachwoods, which may have been used for the purpose of adulteration, leaving nothing on the cloth but the madder colours.

The author had several instances of adulteration by dyewoods, during his long experience in Manchester, but the most difficult case which came under his notice occurred some years ago. Several samples of madders were submitted to him, whose dyeing power was so inferior that undeniably some adulteration had been practised; still, the amount of ash was right, and no foreign dyewood could be detected. After a great number of experiments it was ascertained that they had been mixed with spent madder.

Garancin and *fleurs de garance* are tested in the same way, but eight grains only are taken, and the specimens are only heated to 180° F.

The extracts containing much more colouring matter than madder or garancin, it is better to use six inches of cloth in place of three, and two quarts of water, taking only two grains of the extract.

With Dutch and Alsace madders it is necessary to make a second trial, adding 1 or 2 per cent. of chalk to neutralise the acids naturally present and to combine with the injurious colouring principles.

Garancins also are often not sufficiently washed. It is necessary, therefore, to ascertain if they are perfectly neutral, and if not, to add chalk in this case also.

In the case of garancins, *fleurs de garance*, and extracts, if the operation has been properly conducted, the whites will be clear without soaping. If they are not satisfactory, they may be cleared by heating with water containing 10 per cent. of bran for about ten minutes at 180° F.

M. Pernod, a few years ago, published a very simple and practical method for ascertaining if a sample of garancin or madder is adulterated with sapan or peachwood, logwood, fustic, or valonia or other tannin matters.

His process consists in dipping a sheet of paper in a weak solution of bichloride of tin, and another in persulphate of iron. These papers are each placed on a plate and the suspected sample sprinkled over them. If any of the woods are present, the tinpaper gives with sapan or peachwood, crimson; with logwood, purple; and with fustic or bark, yellow spots. The iron paper gives, with logwood, black; and with valonia or any other tannin matter, dead black spots.

To ascertain if the reds, pinks, purples, or chocolates on a piece of calico are derived from madder, the following tests may be applied.

1. A small piece of the fabric is calcined. If it is a madder red or pink it will leave a white ash of alumina, soluble in concentrated sulphuric acid. The solution thus obtained when diluted with water yields a white gelatinous precipitate on the addition of ammonia.

If it is a madder purple it will leave a reddish residue, soluble in hydrochloric acid, and containing iron; the solution when diluted will give a blue precipitate with potassium ferrocyanide (yellow prussiate). Madder chocolates will yield an ash of an ochre colour from which the iron may be dissolved by treatment with hydrochloric acid, and if the residue be heated with concentrated sulphuric acid and the solution diluted, it will give the characteristic tests for alumina. If the chocolates yield a green ash, chromium



has been used. If the ash be fused with borax before the blowpipe it will yield a green bead, and with nitrate of potash it will form potassium chromate. This on being dissolved in water will give a bright orange or yellow precipitate with salts of lead.

2. If a piece of the dyed cloth be dipped in a solution of bleaching powder it will be decolourised, but if carefully washed and placed in a bath containing madder and gradually heated the original colour will reappear.

3. If dipped in hydrochloric acid the colour on the cloth assumes an orange hue, which in contact with milk of lime becomes changed to purple. It will stand passing through a weak soap bath at 180° F. This character may be observed with reds and chocolates as well as with purples.

Garancin work gives all the above characters, but the colours will not stand a rather strong soap solution.

The properties of the colouring principles of madder have been somewhat fully described, as well as the methods employed in rendering them available for dyeing fabrics, because these colours have been so long known, are so durable, so extensively employed, and so interesting from a scientific point of view. The *rubia tinctorum*, however, is not the only species of *rubiacæ* which yields fast colours with the ordinary mordants, or even with cloth oiled, as in the Turkey red process. There are two other important dyestuffs obtained from this natural order, namely, *munjeet* and *chayaver*, which may be briefly described here.

It is to the researches of Dr. Stenhouse that we are indebted for the information we possess on the colouring matters of *munjeet* or *rubia munjista*. This peculiar variety of the genus *rubia* is cultivated exclusively in Asia, and especially in India, where it has been used as a dyestuff from a remote period, either alone or mixed with other dyes, to produce a variety of red shades. It is imported

into this country from time to time, but has never been very extensively used, as the colours produced from it are neither so bright nor so fast as those obtained with the *rubia tinctorum*.

Whilst the colouring principles of madder are purpurin and alizarin, those of munjeet are purpurin and a yellow colouring matter, named by Dr. Stenhouse, *munjistin*.  $C_8H_6O_3$ . This latter body, which in some specimens is present only in very small quantity, crystallises from its alcoholic solution in beautiful golden-coloured scales: when slowly sublimed it forms golden scales and broad flat needles of great beauty. It is only slightly soluble in cold, but freely in hot water. It gives with caustic soda a rich crimson colour. Alumina removes it entirely from its aqueous solution, and the orange-coloured lake so formed communicates to soda the crimson colour above mentioned.

To obtain the colouring matter from the munjeet, one part of the finely powdered root is boiled for four or five hours with two of sulphate of alumina and sixteen of water. The red liquor thus obtained is strained through a cotton cloth and hydrochloric acid added; as the liquid cools a bright red precipitate is thrown down. This is collected on a filter, well washed, dried, and treated with bisulphide of carbon, which dissolves the colour-giving principles, thus separating them from the dark-coloured resinous impurities. When the bisulphide is distilled off it leaves a residue consisting of purpurin and munjistin, from which the latter may be dissolved out by treating it with boiling water. On the addition of hydrochloric acid to the aqueous solution the munjistin is separated in orange-coloured flocks. This precipitate is collected and dissolved in alcohol, which when concentrated by distillation yields the munjistin in a crystalline state; after two or three crystallisations, it is quite pure.

According to Mr. Higgin, the munjeet root yields from

52 to 55 per cent. of a garancin, which has only half the dyeing power of the garancin made from madder. It cannot, therefore, be used with advantage for this purpose.

The inferiority of munjeet arises from its containing only the comparatively feeble colouring matters, purpurin and munjistin. Munjeet is not much used by calico printers, as the munjistin, when present, gives a brownish-purple with salts of iron, which prevents it being employed with that mordant. It is principally used for special shades of Turkey red.

Munjeet is an excellent source of pure purpurin as it contains no alizarin, but only a mixture of purpurin and munjistin, the latter of which can easily be removed by thoroughly washing the purified mixture of colouring matters with boiling water. After this treatment, one or two crystallisations from boiling spirit yield pure purpurin in deep crimson needles. In the mixture of colouring matters obtained from madder, on the contrary, the purpurin is associated with alizarin and various other substances from which it is a matter of extreme difficulty to separate it in a pure state.

The chayaver is not used in Europe, owing to its only containing one-fourth of the amount of colour-giving principle which can be obtained from madder roots, but it is extensively cultivated and used on the coasts of Malabar and Coromandel, to obtain red colours on cloth oiled in a similar manner to that employed for Turkey red. Chalk is added to the dyebeck, which is heated at first to about 100° F. for some time, and afterwards carried to the boil to fully develop the colour. The brilliancy of the colour is brought out by heating the goods in a weak soap solution in closed vessels.

This root gives all the colours obtainable with madder, and like madder colours, they can stand soaping.



Kœchlin and Schunck find that alizarin can be easily extracted from this root by means of alcohol.

Two more varieties of rubiaceæ are also used in the East, one of which bears the name of nona, the other is called ouongkondou; the former is very acid, and contains a large quantity of a yellow colouring matter.

The last source of the colouring principles of madder which will be mentioned is the *morinda citrifolia*, the 'Al' root, or Sooranjee of the Hindoos, who employ it in a Turkey red process. The fabric is steeped in an emulsion of sesam oil, exposed to the air, and then dyed with the pulverised root. This plant is extensively used as a dyestuff in the Madras Presidency. Whilst munjeet contains purpurin but no alizarin, this plant contains alizarin but no purpurin.

In 1829, Anderson examined this root, and obtained from it a pale yellow crystalline body, which he called morindin. This compound on distillation yields a reddish-yellow crystalline sublimate, to which he gave the name of morindone. Stenhouse has since examined these compounds, and the results he has obtained are contained in the following note.\*

"In 1852, Professor Rochleder, from the consideration  
"of Anderson's statement, gave it as his opinion, that  
"morindin was identical with the ruberythric acid which he  
"himself had obtained from madder, and that morindone  
"was alizarin. About eighteen months ago I was fortunate  
"enough to obtain a very small quantity of 'Al' root, from  
"which I extracted the morindin by Anderson's process.  
"When cautiously heated in a Mohr's apparatus, it was  
"decomposed, yielding a sublimate of bright yellowish-red  
"needles, which had all the physical and chemical proper-  
"ties of alizarin.

"When powdered morinda root is boiled with moderately

---

\* Jour. Chem. Soc., xvii., 333.

"dilute sulphuric acid, as in the ordinary garancin process, "its morindin is converted into alizarin; but the large "quantity of brown resinous matter which is produced at "the same time, very greatly diminishes the value of the "dyestuff obtained, for it renders the colours dull and "the whites very difficult to clear. Although 'Al' root is "therefore never likely, at least in Europe, to compete "successfully with madder, still it furnishes the scientific "chemist with the best known source of *pure* alizarin; "for, as is well known, it is by no means easy to separate "the last trace of purpurin, which always accompanies "alizarin in ordinary madder."

## CHAPTER IV.

### RED DYEWOODS, SAFFLOWER, AND ALKANET.

RED DYEWOODS.—In this chapter an entirely different class of red, purple, and black colours will be described, which, although like madder derived from the vegetable kingdom, are obtained not from the roots of an herbaceous plant, but from the stems of trees which attain a considerable size; they are known in commerce under the name of dyewoods. These have been very extensively used for a considerable time, and although the brilliant shades of the coal-tar colours have in some measure superseded them in certain branches of dyeing, yet the rapid increase of the dyeing trade has prevented any diminution in the actual amount imported into and used in this country.

LOGWOOD.—The first, both in importance and in order of the time of its introduction, is campeachy or logwood, which is obtained from a large tree of the leguminous family, called by the botanist *Hæmatoxylon campechianum*, growing abundantly in the West Indies, Mexico, and other States of South America. The finest wood was formerly imported from the bay of Campeachy, in the gulf of Mexico, but as this source of supply is now almost exhausted, the best commercial qualities are at present obtained from Jamaica and St. Domingo, whilst Honduras, Martinique, and Guadaloupe furnish woods of inferior quality.

Campeachy wood was introduced into Europe by the Spaniards, but it was not until the reign of Elizabeth that it came into use in England, and then only for a short time; for upwards of a century its employment was for-



bidden under the most severe penalties, on the grounds that the colours it produced were fugitive and easily injured by weak acids and by the action of the atmosphere. About the fourteenth year of the reign of Charles the Second, however, these penalties were repealed, for it had been found that by the use of various species of tannin the stability of the logwood colours was much increased and their brilliancy heightened.

On the appointment of M. Chevreul to the post of professor of chemistry to the Gobelins, that eminent chemist turned his attention to the study of the various colouring matters and colour-giving principles of the dyestuffs. Among the first to engage his attention was logwood, in which (in the year 1810) he discovered a crystalline substance of a yellowish-white colour, having a prismatic form, and becoming rapidly coloured on exposure to the atmosphere, especially if a trace of ammonia were present. He gave to it the name of *hæmatin*. Erdmann, in 1842, examined it further, and changed the name to *hæmatoxylin*, by which it is now generally designated. It is only slightly soluble in cold water, to which it communicates a bitter sweet taste. It is more soluble in hot water, and is readily dissolved by alcohol, ether, and bisulphide of carbon. It combines with three molecules of water, forming a crystalline hydrate, which at 212° F. still retains one molecule. The formula of these compounds may be thus expressed:—



Hæmatoxylin assumes a beautiful purple colour when exposed to the action of oxygen, especially in the presence of alkalis, being converted into a compound called hæmatëin.

Erdmann prepared this product by saturating ammonia

with hæmatoxylin, and leaving the solution exposed to the air for some time; the liquor assumed a dark cherry-red colour, and gradually yielded small crystals, which he called hæmatëate of ammonia. On decomposing this compound with acetic acid a bulky brownish-red precipitate was obtained, which on desiccation acquired a metallic greenish lustre.

Hæmatëate of ammonia may be obtained in four-sided microscopic prisms of a violet-black colour, which lose their ammonia at  $212^{\circ}$  F.

Erdmann finds that hæmatëin prepared by this process is more soluble in alcohol than in water or ether, and that when dissolved in ammonia and left in contact with the air it becomes brown, and at last nearly black, showing that hæmatoxylin may undergo several degrees of oxidation.

Reun, who has recently studied this substance, states that it may be obtained in crystals by exposing to the air an ethereal solution of hæmatoxylin, to which a small quantity of concentrated sulphuric acid has been added. After some time brownish-red crystals are deposited on the sides of the vessel containing the liquid. These must be collected and washed with ether. The crystals are soluble in hot water, which on cooling solidify to a gelatinous mass; this, on the evaporation of the water, leaves amorphous scales, having a cantharides green lustre. These scales dried in the air give, on analysis, results corresponding to the formula  $C_{16}H_{12}O_6 + 3OH_2$ . The crystals dried in vacuo have the composition  $C_{16}H_{12}O_6 + OH_2$ , and when dried at  $212^{\circ}$  F.  $C_{16}H_{12}O_6$ .

This compound cannot be recrystallised from an alcoholic solution; ammonia and the other alkalis colour it a fine violet-blue. It can easily be reconverted into hæmatoxylin by boiling its solution with sulphurous acid, or with zinc and sulphuric acid, or by the action of sulphuretted hydrogen.

The following equation represents the manner in which the hæmatoxylin is converted into hæmatëin by oxidation:



When perfectly pure, hæmatoxylin is quite white, and readily enters into combination with the alkalis. A colourless barium compound may be obtained, which, however, rapidly becomes purple on contact with oxygen, as do also the potash and soda salts; this effect is due to the conversion of the hæmatoxylin into hæmatëin.

The oxidation and consequent colouration of hæmatoxylin, under the influence of alkalis, is so rapid that it may be used as a most delicate test for the presence of carbonate of lime in natural waters; and it is a fact well known to practical dyers that water containing a large quantity of carbonate of lime is well adapted for the production of logwood blacks, not only because it accelerates the oxidation of the iron mordant and the fixing of it on the tissue, but also because it facilitates the oxidation of the hæmatoxylin and consequently its conversion into hæmatëin, the former giving little or no colouration with salts of the protoxide of iron, whilst the latter gives a dark purplish-blue.

Reun found that the action of caustic potash on hæmatoxylin gives rise to pyrogalllic acid. Four parts of potash and one of hæmatoxylin are fused together until the mass acquires a brown colour; the product is dissolved in water, neutralised with dilute sulphuric acid, filtered, and agitated with ether. On evaporating the ethereal solution a syrupy residue is left, which yields a crystalline sublimate of pyrogalllic acid when submitted to distillation. The occurrence of this benzene derivature and others closely allied to it, in the products of the action of caustic alkalis on many of the colouring matters, shows an intimate connection between them.

Mr. Sorby has given, in the proceedings of the Royal Society, vol. xv., the characters which the various colours



present when examined with the spectroscope; but, as the paper bears on the analysis of colours generally, it will be preferable to give a *résumé* of it under that head, rather than describe the spectrum of each colour, as it passes under our notice.

Logwood yields but a small amount of colouring matter to cold water, and to boiling water only about 3 per cent. With distilled water the decoction has only a pale yellow tint, and with a calcareous one a blood-red colour. The whole of the hæmatoxylin, however, can only be removed with difficulty by means of water, but alcohol and ether dissolve it with facility. Large prismatic crystals of the colouring matter are often found at the bottom of casks in which logwood extracts have been kept for a considerable time. An aqueous solution of hæmatoxylin gives the following reactions :—

|  |   |
|--|---|
| Weak acids                                 | The colour changes to yellow.   |
| Concentrated acids                         | The colour changes to red.  |
| Sulphuretted hydrogen                      | { Becomes yellow and is then decolourised.  |
| Soluble alkalis                            | { Colour it of a reddish-purple, which becomes violet more or less tinted with blue.                                |
| Lime water                                 | Blue precipitate.   |
| Neutral salts of magnesia, lime, or baryta | { Colour the liquid purple or violet.   |
| Alum                                       | { First becomes yellow, gradually changing to wine colour and violet, and then gives a purple precipitate.          |
| Bichromate of potash                       | Black colouration.  |
| Salts of lead                              | { Very dark violet precipitate, more blue than red by reflected light, and more red than blue by transmitted light. |

|                     |                                  |
|---------------------|----------------------------------|
| Chloride of tin     | Violet or blue precipitate.      |
| Salts of iron       | Bluish-black precipitate.        |
| Salts of copper     | Dark-blue or violet precipitate. |
| Salts of zinc       | Dark reddish-purple precipi-     |
| Salts of gold       | Orange precipitate. [tate.       |
| Chloride of mercury | Orange-red precipitate.          |
| Nitrate of bismuth  | Magnificent violet precipitate.  |

It is highly probable that the colour-giving principle exists in *Hæmatoxylon Campechianum*, in the state of a glucoside, for when the trees are felled the wood is colourless; but by the time the logs arrive in this country the outside is of a dark red colour, whilst the inside is only pale yellow. This is no doubt due to the hæmatoxylin glucoside being partially decomposed, and the hæmatoxylin being converted into hæmatëin on that portion of the wood exposed to the air. As it is the latter substance the dyer requires, it is necessary to effect the complete decomposition of the glucoside, and the oxidation of the hæmatoxylin. The plan adopted is to rasp the logs as imported into a coarse powder, and after moistening it, to lay it in beds 15 to 20 feet long, 10 to 12 feet broad, and about 3 feet thick. A slow fermentation ensues, during which the glucoside is decomposed and the hæmatoxylin liberated. The beds are frequently turned, both to allow the air to act on the hæmatoxylin and to prevent the fermentation proceeding too rapidly, or the heap from getting too warm, in which case the colouring matter would be completely destroyed. The ammonia liberated from the azotised principles of the wood during the fermentation no doubt greatly facilitates the formation of the colour.

Logwood thus prepared is used not only directly by the dyer to produce logwood blacks, but also to prepare an extract much used in calico printing and woollen dyeing.

To obtain a good extract it is important that the powder should not be too highly oxidised, and that the solutions obtained by repeated lixiviations should be slowly concentrated at a comparatively low temperature, that is to say not exceeding 150° F., for if a high temperature be employed the hæmatëin undergoes further change, and is converted into a dark purple resinous principle, which spoils the brilliancy of the colour and of course materially decreases the value of the extract. For this reason many printers prefer to use the decoction, which they make as they require it, and it is doubtless on this account that the dry extracts of logwood which have from time to time been imported into this country have had so little success. One of the best methods of concentrating the liquid consists in evaporating the decoction of the logwood on a double copper cylinder, 4 or 5 feet in diameter, and heated by steam; this, which dips into a trough containing the extract, is kept slowly revolving. By this means a large surface for evaporation is obtained, whilst the temperature can be kept at the low point which is essential for the production of a good extract.

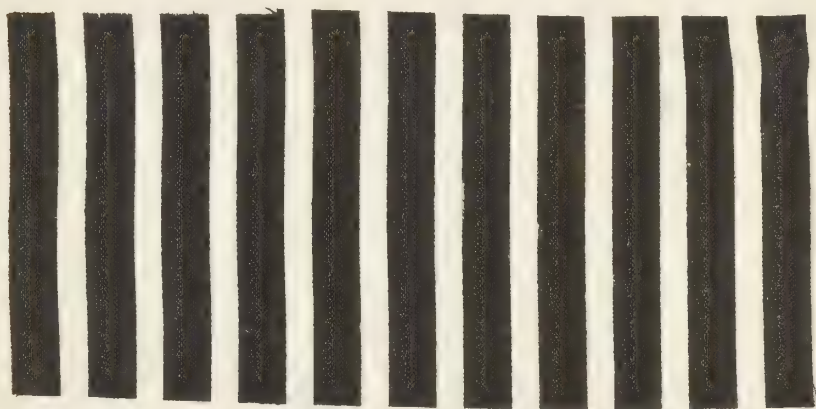
To produce purples and violets, in steam styles, the cloth is passed through a solution of stannate of soda, and afterwards through a bath of dilute sulphuric acid; or first through a solution of oxymuriate of tin, and then through a dilute alkali bath, by which means stannic oxide or bin-oxide of tin is separated and fixed as a mordant in the fibre of the cloth. After the fabric has been washed and dried, a strong solution of logwood thickened with starch is printed on it, and it is again dried by passing over steam cylinders. It is now either rolled on a perforated cylinder and submitted to the action of high-pressure steam, or hung in an iron chamber and steamed at a low pressure, when the hæmatëin combines with the oxide of tin, producing a beautiful purple.





LOGWOOD PURPLE.

For the production of blacks the fabric is printed with pyrolignite of iron, exposed to the atmosphere and treated in a manner similar to that employed for fixing the iron mordant for madder, which has been already described. It is then padded in a logwood solution, and the black afterwards fully developed by passing it through a hot dilute solution of bichromate of potash.



LOGWOOD BLACK.

Logwood and its extract are also much used in Yorkshire for producing cheap blacks on mixed fabrics, that is,

goods in which the warp is cotton and the weft woollen. The fabric is dyed in a bath composed of logwood, sulphate of soda, and bichromate of potash; and the black so produced is the fastest that can be obtained with logwood; part of the oxygen of the bichromate oxidises the colouring principle, and the sesquioxide of chromium which is thus produced becomes fixed on the fabric and acts as a mordant.

Besides being used for dyeing blacks, as above stated, it is also employed to produce greyish purples with salts of alumina. It is likewise extensively used for dyeing silk and leather as well as for cotton and wool.

BRAZIL, PEACH, SAPAN, AND LIMA WOODS.—All these woods are obtained from trees of the genus *Cæsalpinia*, belonging to the natural order *Leguminosæ*. They are imported into this country in sticks or logs, varying considerably in size, of a dark red colour externally, but nearly colourless in the interior; they have a slightly aromatic odour and a bitter sweet taste, freely colouring the saliva. As they grow in dry and rocky formations their wood is generally crooked and knotty.

Although these woods have long been employed as dye-stuffs in the countries where they are grown, it is only since the introduction of Brazil wood by the Spaniards that their value has been fully appreciated in Europe.

*Brazil wood*, derived from the *Cæsalpinia Brasiliensis*, grows in the forests of Brazil, and may be considered as the best of this class. It has become somewhat scarce in the market from its having been all cut in those districts which are within easy distance of shipping ports.

The wood most in favour at the present day is the product of the *Cæsalpinia Crista*, and is imported from Parahiba, Pernambuco, and Jamaica, and is known as Pernambuco or Pernambuco wood.

*Peachwood*, sometimes also called Santa-Martha wood,



derived from the *Cæsalpinia echinata*, is imported from Nicaragua, and an inferior quality from Sierra Nevada.

*Sapan wood*, the product of the *Cæsalpinia sappan*, is imported from Siam, Japan, the East Indies, and other Eastern countries.

*Lima wood*, an inferior variety, is imported from Peru. Other woods of the genus *Cæsalpinia*, known in commerce as California wood, Bahia wood, Jamaica wood, and Sierra Firma wood, are also imported to this country from various parts of South America.

All these woods give very similar shades of colour on fabrics, either when employed alone or with mordants; so that it would appear that they contain the same glucoside, which is decomposed by peculiar ferments into a saccharine matter and a colour-giving principle. That this inference is correct is proved by the following experiments:— If the decoction obtained by treating the wood from the interior of the logs be boiled with a solution of double tartrate of potash and copper (the best known test for grape sugar), no precipitate is obtained; whilst if it be first boiled with dilute sulphuric or hydrochloric acid (which would decompose a glucoside), and afterwards treated with the copper salt, an abundant precipitate of the suboxide of that metal is thrown down. Although the original solution, which has only a faint yellow colour, gives no precipitate with acetate of lead, yet after it has been boiled with acid it gives an abundant precipitate of a brilliant brick-red colour. If a concentrated solution is neutralised, after having been boiled with an acid to decompose the glucoside, it deposits on cooling a small quantity of the colouring principle in beautiful reddish crystals. No such crystals can be obtained from the original solution.

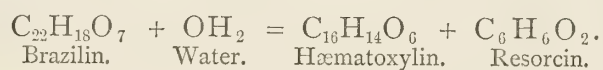
The colour-giving principle which appears to be the same in all these woods was first obtained from Brazil



wood, by Chevreul, who gave it the name of *brazilin*. It forms needles which are nearly colourless, and which have a bitter sweet taste.

In 1865, Messrs. Müller & Co., of Basle, placed in the hands of Professor Bolley, some very large crystals which had been deposited at the bottom of casks, in which an extract of sapan wood had been kept for a considerable time. These proved to be brazilin soiled by a little brazilëin. By crystallisation from alcohol he succeeded in obtaining pure brazilin in the form of oblique rhomboidal prisms, having a diameter of about one-tenth of an inch. These are freely soluble in alcohol and ether, and on analysis were found to have the formula  $C_{22}H_{20}O_7 + 3OH_2$ . At a temperature somewhat below  $212^\circ$  F. it loses the three molecules of water.

According to E. Kopp,\* however, the formula of anhydrous brazilin is  $C_{22}H_{18}O_7$ , and its relation to hæmatoxylin may be expressed in the following manner :



He finds that the crust, which is obtained in considerable quantity in the manufacture of Brazil wood extract, contains much brazilin, and brazilin lime lake. On treating it with dilute hydrochloric acid to remove the lime, and then boiling it with a mixture of one part of alcohol and eight of water, a solution is obtained from which brazilin crystallises out on cooling. It is well known that extract of sapan wood when treated with nitric acid yields styphnic acid, which is identical with the trinitroresorcin, produced by the action of nitric acid on resorcin. Moreover, Schreder,† by fusing extract of sapan wood with potassium hydrate, has obtained resorcin; at the same time pyrocatechin is produced, and also a cystallisable substance, *sappanin*, to

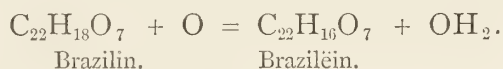
\* Deut. Chem. Ges., Ber. vi. 446.

† Deut. Chem. Ges., Ber. v. 572.

which he assigns the formula  $C_{12}H_{10}O_4, 2OH_2$ . It dissolves in boiling water, and crystallises out again on cooling. It possesses no marked characteristics.

A solution of brazilin when exposed to the atmosphere acquires a brilliant red colour, and is slowly oxidised to brazilëin; this action may be much accelerated by heating the liquid, especially in the presence of alkalis. On allowing the solution to evaporate, beautiful red needles are deposited, having a satiny lustre.

The change, which is analagous to that which takes place with hæmatoxylin, may perhaps be represented by the following equation:



Brazilëin dissolves freely in water, alcohol, and ether. It is easily reduced to the colourless brazilin by boiling its solution with bisulphite of soda.

According to Reun, a crystalline brazilëin may be obtained from brazilin, in a manner precisely similar to that described when treating of the conversion of hæmatoxylin into hæmatëin.

On adding chromic acid or bichromate of potash to a concentrated solution of brazilin the liquid assumes a dark brown colour, and in a little while a very dark crimson lake separates, which is a compound of brazilëin with oxide of chromium. This compound is not very stable, as it is easily decomposed by dilute hydrochloric acid. This reaction illustrates the use made of bichromate of potash by the calico printer when dyeing with these woods.

A decoction of any of these woods becomes yellow or orange (according to the quantity of brazilin or brazilëin it contains) on the addition of an acid; by the aid of heat the conversion of the brazilin into brazilëin is hastened, and it is the latter compound the dyer and printer require. The transformation is still more rapidly effected by the

addition of a small quantity of potassium bichromate or chlorate. Great care, however, is required in using these salts, for if too much be added a brown, resinous, nearly insoluble product is formed, which injures the brilliancy of the colour; this may occur also in the preparation of the extract if the operation is not carefully conducted. The addition of an alkali to a decoction of the wood produces a magnificent crimson-red, varying in shade according to the proportion of the two principles present.

The following reactions will serve to characterise decoctions of these woods :—Acids turn them yellow, of a more or less orange shade, the shade varying with the variety and state of oxidation of the wood from which the decoction is prepared; after a certain time crystals are separated, which are yellow if the decoction is not much oxidised, but red if the contrary be the case. It seems probable that these crystals are deposited on account of the splitting up of the glucoside into sugar and the colouring matter, and the latter, being comparatively slightly soluble, separates in the crystalline state. An excess of strong hydrochloric acid alters the shade to a bright pink, but it disappears on the addition of water. The alkalis, caustic or carbonated, give a crimson-red tint. Chromate of potash, as already mentioned, gives a dark red liquor, which on standing deposits a deep red precipitate. Neutral acetate of lead only gives a slight reddish precipitate. The filtered liquor, although almost colourless itself, dyes with a deeper shade than the original liquor. It appears, therefore, that acetate of lead merely precipitates the superoxidised matters and the substances which injure the beauty of the colour. Sub-acetate of lead gives an abundant bluish precipitate. These tests are sufficient to characterise the Brazil wood colours.

To prepare a good commercial extract from the woods they must be finely ground, as they yield their colour to water with difficulty; like logwood, they should be allowed

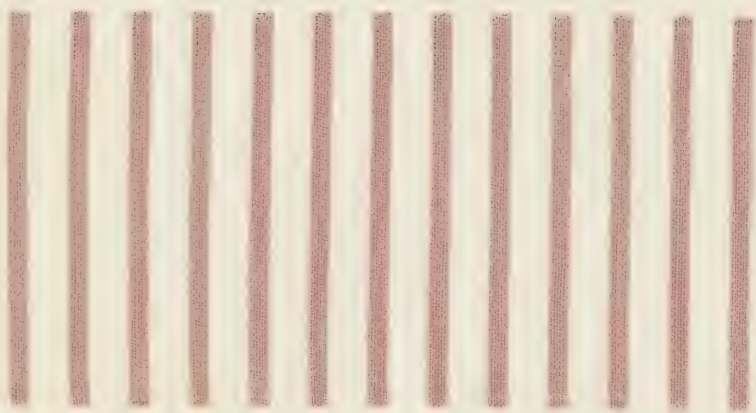


to ferment and partially oxidise in the air before being treated with water, but not to the same extent; the more quickly the solutions are evaporated the brighter is the colour produced. From a ton of sapan wood there is usually obtained about 640 gallons of liquor, marking about  $2\frac{3}{4}$  Twaddle, and this is evaporated to 150 gallons, marking 7 to  $7\frac{1}{2}$  Twaddle. The apparatus employed consists of a double copper vessel or trough, the space between being supplied with steam; in this revolves also a copper steam cylinder. By this arrangement a very large amount of heat is imparted to the liquid placed in the trough, and the steam given off in the evaporation prevents the over oxidation of the extract. With a machine, having a cylinder 4 feet 8 inches long by 2 feet 6 inches in diameter making twelve revolutions per minute, with steam at a pressure of 30 lbs., 640 gallons can be evaporated to 150 in ten hours. If the finely rasped wood be exposed to strong sunlight for twelve months it no longer yields any colouring matter.

Dingler's process for the preparation of an extract from these woods is said to give very good results. It consists in adding 4 lbs. of gelatin dissolved in water to every cubic yard of ground wood, and allowing the whole to ferment for several days. Wood so treated yields a stronger and richer extract than that obtained by the ordinary process; it is possible that the gelatin assists the decomposition of the glucoside, and that the ammonia produced by the putrefaction of the animal substance facilitates the oxidation of the brazilin. Mr. Peak, some years ago, found that the addition of a small quantity of chlorate of potash to the hot extract greatly increased its brilliancy and rendered it more valuable to the printer on account of the brighter colour produced on the fibre.

These extracts give with iron and alumina mordants colours similar to those obtained with madder, namely,

purple with salts of iron, red with salts of alumina, and chocolate with a mixture of the two, but they are principally used to obtain pinks and reds in steam styles. To effect this acetate of alumina, chloride of tin, oxalic acid, or acetate of copper is added to the extract and printed on prepared cloth, as already described, which is then submitted to the action of steam. The fastness of the colours so produced is much increased by adding a little sumach extract to the wood solution. M. K. Koechlin, of Alsace, has been kind enough to supply the accompanying sample, illustrating the effect obtained with Brazil wood.



BRAZIL WOOD ROSE COLOUR.

The extracts are also used in conjunction with a little quercitron or bark in the production of cheap garancin styles. These inferior garancin prints are easily distinguished from the good ones by means of a hot soap bath, which only slightly affects the latter whilst the former are almost entirely destroyed. The woods themselves also are sometimes used for the adulteration of garancin.

Before leaving this subject it may be stated that decoctions of these woods yield very beautiful pink lakes, much

used by decorators and paper stainers under such names as Venetian, Florence, or Berlin lakes. Most of them are obtained by saturating a strong decoction of wood with a mixture of chalk, starch, and a little alum, pressing the whole into cakes and drying them. Venetian lake, the best of the class, is prepared by mixing a decoction of Brazil wood with gelatinous alumina and gelatin, and brightening the tint by the addition of a little alum in solution; the mass is then dried. If it is wished to have a purple lake a certain proportion of soap is added before drying. Common red ink is also prepared by adding a little alum and acid to a decoction of these woods.

SANDAL, BAR, AND CAMWOODS.—The dyestuffs of the next class, which are almost insoluble in water, are derived from several varieties of the genus *Pterocarpus*, which are indigenous to the tropical parts of both the new and the old world.

*Sandal wood*, called also *Santal* or *Sanders wood*, the produce of the *Pterocarpus santalinus* is much used in India as a dyestuff. It is imported into this country from the East Indies, Ceylon, Madagascar, and the coasts of Coromandel and Malabar, and consists of large billets which have a compact and hard appearance, and a dull, murky, red colour. It is more used on the continent than in England, and yields to alcohol about 16 per cent. of colouring matter, insoluble in water.

*Barwood* is the wood of a fine tall tree, called *Baphia nitida*, growing in great quantities at Sierra Leone. It yields to alcohol about 23 per cent. of colouring matter, but cold water extracts very little, and boiling water only about 7 per cent. Acetic acid and alkalis dissolve out the colouring matter.

*Camwood*, or Kambe wood, is a dyewood very closely allied to the two just mentioned, and is also imported from the west coast of Africa. Owing to its price being higher



than that of barwood it is not extensively used, and its general properties and the character of its colouring matter have not been much studied.

The colouring principles which these three dyewoods contain appear to be very similar, if not identical. It is only developed by age, not being found in the young branches, whilst it exists in large quantities in the trunk. Pelletier first isolated the colouring matter from sandal wood under the form of a red resin. Preisser stated that he had obtained it as a white crystalline mass, by mixing hydrated oxide of lead with an ethereal solution of the wood, and after well washing the lake thus formed, decomposing it by sulphuretted hydrogen; the product was then heated with ether, and the ethereal solution evaporated in vacuo. According to Meier, sandal wood contains four substances soluble in water, and two which are insoluble, namely, santalic acid and santalin. He prepares the latter by exhausting the wood with ether, and evaporating the ethereal solution, when it leaves the impure santalin in a crystalline state. After washing it with water it is dissolved in alcohol and precipitated with lead acetate. The lead compound is then thoroughly washed with boiling alcohol, and decomposed by dilute sulphuric acid. Thus obtained it forms small bright red crystals, having the formula  $C_{15}H_{14}O_5$ . (?)

The colouring matter of sandal wood is insoluble in cold water, very slightly soluble in hot water, but soluble in alcohol, ether, and acetic acid. The latter solvent yields the colouring matter to albumen, which is an important fact, and may one day be rendered practically useful. Santalin is freely soluble in alkaline solutions, giving a violet-red liquid, from which acids precipitate the colouring matter in red flakes. Bolley considers that the wood contains two principles, one containing more oxygen than the other, and two equivalents more hydrogen.

Weidel,\* who has recently studied the nature of the colouring matters of sandal wood, has succeeded in isolating two crystalline substances; one of these, *santal*, is colourless, and is perhaps identical with the santalin of Preisser; the other, *santalin*, is a bright red compound, and is probably the santalin of Meier, Westermann, and Haeffely.

Santal is obtained by treating the wood with a weak alkaline solution, and then neutralising the extract with hydrochloric acid, which throws down a precipitate. This, after being collected, washed, and dried, is exhausted with ether. The ethereal solutions are then mixed with alcohol and the whole allowed to evaporate spontaneously. In the course of a few days nearly colourless crystals of santal are deposited, which only require to be washed with a little alcohol to be quite pure.

Santal crystallises from hot alcohol in colourless, lustrous plates, having the formula  $2C_8H_6O_3 + 3OH_2$ . They are tasteless, inodorous, insoluble in water, bisulphide of carbon, benzene, and chloroform, and only slightly soluble in alcohol and ether. Its alkaline solution has a yellow colour, which becomes rapidly red in contact with the air, and gives a red precipitate with salts of lime and baryta. Its alcoholic solution assumes a dark red colour with perchloride of iron. When fused with caustic potash it yields protocatechuic acid according to the following equation:—



A thousand parts of wood yield three parts of santal.

If the wood which has been acted on by alkalis is treated with ether and the solution evaporated, it deposits a red substance, which as the ether evaporates assumes a crystalline form. It has a magnificent scarlet colour, with a green metallic iridescence, and is the santalin of Weidel.

---

\* Zeits. Chem. [2] vi., 83.

He assigns to it the formula  $C_{14}H_{12}O_4$ , which only differs from alizarin by four equivalents of hydrogen. It is insoluble in water, only slightly soluble in alcohol and ether, and imparts a reddish-purple colour to alkalis.

It will be seen from this short description that, at present, our knowledge of the colouring matters contained in these woods is very imperfect.

Sandal wood is employed, chiefly on the continent, to give a bottom\* to woollen cloth which is to be afterwards dyed with indigo. By this process a very fine blue is produced, called the *bleu de Nemours*, having a purple hue by reflected light. It is also used to impart to woollen and cotton goods a dark red colour, which is changed to a rich brown when passed through a bath of bichromate of potash. With sumach it produces dark browns, and with fustic light browns.

Barwood, which was imported into Europe by the Portuguese, is now extensively used in England for producing on cotton yarns the brilliant orange-red colours known as mock Turkey reds. They are, however, neither so fast nor so bright as the real Turkey red, and are easily distinguished from it by yielding part of their colour to soap, assuming at the same time a purple hue. To obtain the colours the goods are worked for some time in a hot decoction of sumach, then in a solution of protochloride of tin, out of which it is washed first in cold and then in hot water; after this it is put in a bath with the ground wood and kept for some time at a boiling heat until the desired depth of colour is obtained. It is also often used along with other woods in dyeing woollens brown and other dark mixed tints.

---

\*This term is used in dyeing to denote that a colour is applied to a fabric with a view of giving a peculiar hue to a dye which is applied after it.





MOCK TURKEY RED.\*

Camwood is used in a similar manner to barwood, and the colour is considered by many to be both brighter and faster than that of the latter.

The following reactions may serve to characterise an alcoholic solution of sandal and barwoods:—

|   |  |
|---|--|
| Distilled water, added in large quantity, | { Produces a considerable yellow opalescence. The precipitate is redissolved by the fixed alkalis, the liquor acquiring a dark vinous hue.       |
| Chlorine.                                 | { Decolourisation, with brownish-yellow flocculent precipitate, resembling hydrated peroxide of iron, which soon rises to the top of the liquid. |
| Gelatin                                   | { Brownish-yellow flocculent precipitate.  |
| Soluble alkalis.                          | { It becomes dark crimson or violet.   |
| Lime water.                               | { Abundant reddish-brown precipitate.  |

\* We are indebted for this sample to the kindness of Messrs. Wood & Wright.

|                        |   |
|------------------------|---|
| Sulphuric acid.        | { Heightens the colour to a cochineal-red.            |
| Sulphuretted hydrogen. | Acts like water.                                      |
| Protochloride of tin.  | Blood-red precipitate.                                |
| Bichloride of tin.     | Brick-red precipitate.                                |
| Protosalts of iron.    | { Violet colouration and abundant violet precipitate. |
| Persalts of iron.      | { Intense brownish-red colouration and precipitate.   |
| Persalts of copper.    | { Intense brownish-red colouration and precipitate.   |
| Salts of alumina.      | { Merely render the liquid turbid.                    |
| Salts of lead.         | { Dark violet gelatinous precipitate.                 |
| Mercuric chloride.     | Bright red precipitate.                               |
| Nitrate of silver.     | Brownish-red precipitate.                             |
| Sulphate of zinc.      | { Bright red flocculent precipitate.                  |
| Tartar emetic.         | { Abundant dark cherry-coloured precipitate.          |
| Salts of bismuth.      | { Solution coloured bright crimson-red.               |

Camwood differs from the above in the two following reactions:—

|                   |                                |
|-------------------|--------------------------------|
| Salts of lead.    | Bright orange-red precipitate. |
| Salts of alumina. | Beautiful red colouration.     |

There are two other dyewoods closely allied to the above—one called Caliatour wood, imported from the East Indies, which gives even more brilliant colours than sandal wood; the other is from Madagascar, but comes only in very small quantities.

SORGHO.—Sorgho, the *Sorghum saccharatum*, is the Chinese sugar cane, a plant somewhat resembling maize in appearance. It was first grown from seed in France in 1853, and has since been cultivated in France and Germany for the quantity of sugar which it yields. If the pith of

this plant is subjected to pressure, it yields a juice which, when either allowed to ferment, or boiled with dilute sulphuric acid, gives a colouring matter which has received the name of *purpurolëin*, *sorgho carmine*, or *sorgho red*. MM. Sicard, Itier, and Joulie state that the external part of the fruit of the sorgho gives two other colouring matters, *sorghotin* and *sorghin*.

Dr. Winter obtained a colouring matter which may be employed as a dyestuff, by allowing the stems of the plant to ferment until they acquire a reddish-brown colour; when dry they are cut into small pieces and treated with a dilute alkaline solution, from which a red flocculent precipitate is produced on the addition of sulphuric acid. By means of a tin mordant this colouring principle may be fixed on wool and silk.

The Chinese employ the colouring matter produced by fermentation, as a dyestuff to produce colours resembling Turkey red in appearance. The bark of the sorgho contains a yellow colouring matter which has received the name of *xantholëin*.

ALKANET.—Alkanet, the cortical parts of the *Anchusa tinctoria*, is principally imported from the Levant and from South Germany, and contains a colouring principle called by Pelletier, who first isolated it, *anchusic acid*. Bolley and Wydler who some years since examined this root, extracted the colouring matter as a beautiful red resinous mass, and assigned to it the somewhat doubtful formula  $C_{35}H_{40}O_8$ . To prepare it the root is first heated with water to remove all the matters soluble in that liquid, it is then dried and exhausted with alcohol. This solution, which has a violet colour, after being slightly acidulated with hydrochloric acid, is evaporated to dryness, and the residue treated with ether. The ethereal solution on evaporation leaves the colouring matter *anchusin*, or *anchusic acid*, as a dark red resinous mass.



Anchusin is insoluble in water, soluble in alcohol, and very soluble in ether, bisulphide of carbon, turpentine, and the fixed oils.

Alkanet was formerly employed to produce on fabrics various shades of violet, lilac, and lavender, but, on account of its instability when exposed to light, it is now seldom used. Its chief uses are in pharmacy to colour medicines, in perfumery to colour oils and pomades, and in domestic life to give a tint to the lime-wash used for the walls of cottage rooms.

The colouring principle dissolved in alcohol gives a blue colour with alkalis, a purple precipitate with bichloride of tin, a crimson precipitate with protochloride of tin, and a bluish-violet precipitate with acetate of alumina.

ÆNOLIN, or The Red Colouring Principle of Wines. M. Glénard has separated the colouring principle of red wines by the following process:—Subacetate of lead is added to the wine, which produces a blue precipitate: this is collected, well washed, and dried at  $212^{\circ}$  F., and is then treated in a displacement apparatus, first with anhydrous ether saturated with hydrochloric acid gas, and afterwards by ether alone. The solutions thus obtained are evaporated to dryness, and the residue treated with alcohol, which on concentration and the addition of water yields a red flocculent precipitate.

The ænolin thus prepared is insoluble in ether and benzene, only slightly soluble in water, but dissolves freely in alcohol. Its solution in this latter menstruum becomes brown on being boiled for some time in contact with air. The formula assigned to ænolin is  $C_{10}H_{10}O_5$ .

It is also stated that a *blue colouring matter* exists in wines, which is soluble in acetic and butyric acids, and becomes green on contact with alkalis. Some chemists consider it to be identical with the *cyanin* of flowers.

SAFFLOWER.—Although this dyestuff has lost much of

its value since the discovery of the aniline colours, it is still extensively used in Lancashire for the production of peculiar shades of pink for the Eastern markets. It is also used for dyeing red tape, and there is no more striking instance of 'red-tapism' than the love which is shown for this particular colour by the users of that article. Much cheaper pinks can be produced from aniline, but notwithstanding attempts have many times been made to introduce them, they have failed in every instance, because the exact shade has not been attained.

Safflower is the bloom of a peculiar thistle called the *Carthamus tinctorius*, which is indigenous to Egypt and the Levant, but which is now cultivated in France, Spain, Germany, Italy, Hungary, the Southern Asiatic territories of Russia, the East Indies, and South America.

In France and Spain the small flowers composing the heads of the thistle are picked off while in full bloom, and dried in the shade; whilst in Egypt and India the plants are watered morning and evening for several days previously to the bloom being collected, after which the bloom is squeezed, washed with cold water to remove useless matters, slightly pressed into lumps, and dried in the shade; this kind has about double the value of those from other countries.

The safflower so prepared contains only from three to six parts per thousand of the colour-giving principle, which is called *carthamic acid* or *carthamin*. There are also two yellow colouring matters present—one soluble in water, the other insoluble in that menstruum.

M. Salvétat has published the following figures as giving the composition of safflower:—

|   |              |
|---|--------------|
| Yellow colouring matter, soluble in water | 26·1 to 36·0 |
| Carthamin .....                           | ·3 to ·6     |
| Extractive matter .....                   | 3·6 to 6·5   |
| Albumen .....                             | 1·5 to 8·0   |

|                                |              |
|--------------------------------|--------------|
| Wax .....                      | ·6 to 1·5    |
| Cellulose .....                | 38·4 to 56·0 |
| Silica .....                   | 1·0 to 8·4   |
| Alumina and oxide of iron..... | ·4 to 1·6    |
| Oxide of manganese .....       | ·1 to ·5     |

Besides these there is always a certain proportion of pectic acid.

To prepare carthamic acid, safflower is introduced into bags and washed with cold water until all the soluble yellow colouring matter which it contains has been removed, after which it is macerated for two hours in water, in which has been dissolved fifteen parts of crystallised carbonate of soda for every hundred parts of safflower taken. The liquor is then run off; cotton yarn is dipped into it, and lime juice, lemon juice, or citric acid added to liberate the carthamin from its combination with the soda, when it fixes itself in the fibre of the yarn. Up to this point, the process is the same as that adopted in dyeing fabrics, but to obtain carthamin, it is necessary to treat the washed cotton a second time with a weak solution of carbonate of soda, which leaves the second yellow colouring matter fixed on the cloth. The solution thus obtained is acidulated with tartaric acid, when the carthamin falls as a brilliant red, amorphous powder. It may be further purified by solution in alcohol, and precipitation from that menstruum by the addition of water. The safflower extract of commerce is prepared by this method, except that the last precipitation from alcohol is omitted, the red powder being merely mixed with a little water. The red powder when dried and mixed with a little French chalk is employed as rouge.

The formula of carthamin, according to Schlieper\* is  $C_{14}H_{16}O_7$ . A solution of this compound when dried on a polished white surface leaves a varnish having a beautiful

---

\* Ann. Chem. Pharm., lviii., 362.



red colour by transmitted light, whilst it assumes the iridescence of cantharides by reflected light. It is insoluble in water and ether, but soluble in alcohol. On the addition of sulphuric, nitric, or hydrochloric acid, this solution becomes yellow. Alkalis also turn it yellow or orange, and the colouring matter rapidly undergoes alteration when exposed to the air, or when boiled with water or alcohol. It is owing to the fugitive nature of the colour and its easy modification by acid or ammoniacal vapours, that the delicate pinks produced from safflower have been so successfully replaced by the pink aniline dyes.

To obtain the soluble yellow colouring matter already referred to, the aqueous extract of safflower is rendered slightly acid by means of acetic acid, and acetate of lead added. The precipitate thus produced is removed by filtration, and to the clear liquid, ammonia is added in slight excess, which throws down a yellow precipitate. This is collected on a filter, washed, and then decomposed by dilute sulphuric acid. The sulphate of lead so formed is separated, and the aqueous solution evaporated, out of contact with the air. Schlieper assigns the formula  $C_{16}H_{20}O_{10}$  to the yellow colouring matter thus obtained. It becomes brown on exposure to the air. The colouring matter insoluble in water has not been studied.

There is a particular extract extensively used in dyeing, the preparation of which is kept secret. Its value depends on the fact that the carthamin is rendered soluble in water.

This extract, as well as safflower, is employed to dye silk, cotton, and flax in various shades of pink and red. It is used also to produce scarlet shades, in which case the fabrics are first dyed with annatto, then washed, and finally topped with carthamin.

If the safflower is gradually and successively treated first with weak solutions of carbonate of soda, and afterwards with stronger ones, it will be found, that, whilst the first

extract yields the brightest and purest tints, the others will give shades which are progressively inferior. Dyers have taken advantage of this by first dyeing the goods with the coarsest colours from the last extracts, and then topping or blooming them with the bright colour yielded by the first extract.



## CHAPTER V.

### INDIGO.

This most valuable dyestuff was used in India and Egypt long before the Christian era; the Romans also were acquainted with it, although they only used it as a pigment, not knowing how to render it soluble and thereby to avail themselves of it for dyeing. It is only since the sixteenth century, or from the time of the discovery of the passage to India round the Cape of Good Hope, that it has become generally known in Europe; and even then its employment as a dye was greatly retarded by the opposition it met with from the large vested interests of the woad cultivators, who induced the English, French, and German governments to promulgate several enactments against its use. An idea of the severity of some of them may be formed from the fact that Henry IV. of France issued an edict condemning to death anyone who used that pernicious drug called the 'devil's food.' It is only since the year 1737 that the French dyers have had the right to use indigo without restriction.

The plants which furnish indigo do not all belong to the same family, but the most important are leguminous and of the genus *Indigofera*. The most valued and most largely cultivated species are the *Indigofera tinctoria*, *Indigofera disperma*, *Indigofera anil*, and *Indigofera argentea*. Among those less cultivated may be mentioned the *Indigofera pseudotinctoria*, *hirsuta*, *sericea*, *cytisoides*, *angustifolia*, *trifoliata*, *glabra*, *glauca*, &c. These plants appear to be indigenous to the kingdom of Cambay or



Guzerat, but are also cultivated in India, China, Java, and the East. It was also introduced into the West Indies and South America by the Spaniards. The *Indigofera argentea* is chiefly cultivated in Egypt and Arabia. The *indigofera tinctoria*, Fig. 5, is the species most abundantly grown, and is raised from seed which is sown in spring or autumn, according to the variety, the nature of the soil, and the facility of water supply. It is an herbaceous plant, with a single stalk, growing to a height of three feet or three feet six inches, and about the thickness of a finger. It is generally cut for the first time in June or July, just before the plant is in full



FIG. 5.

bloom, a second and third cutting being obtained during the year. When cut it is made into bundles and taken to the factory. The value of the crop is almost in proportion to the abundance of leaves the plant bears, as the colouring matter exists chiefly in that part of the plant.

The Bengal factories usually contain two rows of vats, the bottom of one row being level with the top of the other. Each series numbers from fifteen to twenty, and each vat is about 7 yards square and 3 feet deep; they are built of brickwork lined with stone or cement. About a hundred bundles of the cut indigo plants are placed in each vat, in rows, and pressed down with heavy pieces of wood; this is essential to the success of the operation. Water is then run in so as to completely submerge the plants, when a fermentation quickly ensues which lasts from nine to fourteen hours according to the temperature of the atmosphere. From time to time a small quantity of the liquor is taken from the bottom of the vat to see how the operation is proceeding. If the liquor has a pale yellow hue the product obtained from it

will be far richer in quality but not so abundant as if it had a golden-yellow appearance. The liquor is then run off into the lower vats, into which men enter and agitate it by means of bats or oars, or else mechanically by means of a dash-wheel: each vat requiring seventeen or eighteen workpeople, who are kept employed for three or four hours. During the operation the yellow liquor assumes a greenish hue, and the indigo separates in flakes. The liquor is then allowed to stand for an hour, and the blue pulpy indigo is run into a separate vessel, after which it is pumped up into a pan and boiled, in order to prevent a second fermentation, which would spoil the product by giving rise to a brown matter. The whole is then left to stand for twenty hours, when it is again boiled for three or four hours, after which it is run on to large filters, which are placed over vats of stonework about 7 yards long, 2 yards wide, and 1 yard deep. The filters are made by placing bamboo canes across the vats, covering these with bass mats, and over all stretching strong canvas. The greater part of the indigo remains under the form of a dark blue, or nearly black paste, which is introduced into small wooden frames having holes at the bottom and lined with strong canvas. A piece of canvas is then placed on the top of the frame, a perforated wooden cover, which fits into the box, put over it, and the whole submitted to a gradual pressure. When as much of the water as possible has been squeezed out the covers are removed, and the indigo allowed to dry slowly in large drying sheds from which light is carefully excluded. When dry it is ready for the market. Each vat yields from 36 to 50 lbs. of indigo. The best qualities of indigo are usually manufactured by Europeans, who bestow more care on the operations than the natives. Some manufacturers, in order to facilitate the precipitation, add a little lime water to the indigo when it has been oxidised in the vat by agitation.

J. Sayers, in Djocjocarta, Java, proposes to add ammonia during the fermentation, whereby, he says, that he obtains a purer product.

The other plants which yield indigo are more frequently used directly in dyeing blue than for extracting indigo. The most important are the woad plant, or *Isatis tinctoria*, once extensively cultivated both in England and on the continent; the *Polygonum tinctorium* and the *Herium tinctorium*; the *Asclepias tingens* (of the family Asclepiadæ); *Eupatorium tinctorium* (Compositæ); *Galega tinctoria* (Leguminosæ); and several species of orchids, which, when cut, also become blue at the section on exposure to the air.

Woad, or pastel, Fig. 6, is a biennial plant of the cruciferous order. The leaves are gathered in June in the second year, when the lower leaves are beginning to wither. Others grow in their places and a second crop may be gathered. These leaves are rapidly washed and dried, and used directly for dyeing; or they are made into a paste with water, in heaps of about a yard high, and the fermented mass after fifteen days made into small balls and dried. Sometimes the mass, treated a second time with a little water, is submitted to another fermentation, during which ammonia is developed; the preparation thus obtained is called woad. The best comes from Provence, Languedoc, and Normandy. It is also found in commerce in bales. In Germany the woad of Thuringia is almost exclusively used. Woad is frequently employed in dyeing, mixed with ordinary indigo, as some manufacturers consider that they cannot obtain the finest shades without it. The balls are light, of a sickly odour, and of a green or yellowish-green colour. If cut, it ought to have a soft shining surface, and when rubbed on paper it should leave a green mark. It gains, in tinctorial power by keeping.





THE YOUNG PLANT.



FLOWER.



SEED.



FIG. 6.

The *Isatis indigotica*.—Tein-hoa-tein-ching is grown in most of the provinces of China, for the preparation of a kind of indigo, which is sold as a viscid paste. When dried it has a blackish colour, and is used for the production of Canton blue, &c.

The *Polygonum tinctorium*, Fig. 7, is a herbaceous plant of the family Polygoneæ, also indigenous to China, where a greatly esteemed variety of indigo is prepared from its leaves. It is also used for dyeing directly. Many attempts have been made to acclimatise this plant in Europe, but although they have grown well, the yield of indigo has been too small to make it worth the trouble of cultivation. This was clearly demonstrated by many French chemists in the year 1839.



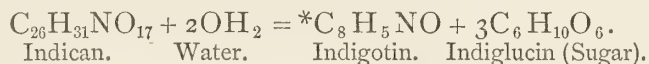
FIG. 7.

The indigo extracted from the various species of *indigofera* varies very much, both in the quantity of pure indigo it contains, and also in its dyeing power. This variation is still further increased by differences of climate, and by the care taken in its preparation. There are thus many qualities known in the market, of which the best are those of Java, Bengal, and Guatemala.

Twenty years ago we had no definite information as to the state in which the colour-giving principle exists in the *indigofera* plant, nor of the changes which it undergoes during the process of extraction. It had been stated by Chevreul, many years before, that the white indigo was held in solution in the plants by the vegetable fluids, and that on coming into contact with the oxygen of the atmosphere it absorbed oxygen, and was converted into the insoluble or blue indigo. In the year 1855, however, and subse-



quently in 1857 and 1865, Schunck published some most interesting papers, in which he described the true nature of the chemical changes which take place in the manufacture of indigo, and proved that indigotin (the colouring matter of indigo), like the colouring principles of madder and the dyewoods, existed in the plant as a glucoside to which he gave the name of indican. Schunck expresses the formula of indican and the decomposition it undergoes as follows :



In his researches on this substance Schunck operated on the *Isatis tinctoria* or woad, which contains the same colouring principle as the indigoferæ, and is the only plant yielding indigo which grows freely in this country. The following was the process he adopted to prove that indican existed in the plant, and was not a product formed either by any chemical reaction, or by the reagents he employed.†

Dried woad leaves were treated with ether, and the ethereal extract poured off into a large bottle and well shaken with half its volume of cold water. The ether was then separated, and the weak aqueous solution of the colour-giving principle agitated with several successive quantities of the ethereal extract, whereby it acquired a yellow colour. The ether it contained was then removed by spontaneous evaporation, and the solution evaporated in a bell-jar over sulphuric acid. The residue consisted of nearly colourless indican, which, when acted on by sulphuric acid, yielded indigo blue. In 1857 he published the following process:‡—Dried woad leaves, after being reduced to powder and carefully sifted, were extracted with alcohol in a displacement apparatus. To the solution thus obtained a little water was added, and it was then concentrated as quickly as possible at the ordinary temperature by passing

\* This formula should be doubled,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ .—Eds.

† Lit. Phil. Soc. Man., 1855, xii., 192.

‡ Lit. Phil. Soc. Man., xiv., 184.



a current of air rapidly over the surface of the fluid. This was done in an ingenious apparatus which he devised for the purpose, and which will be described further on. After a few hours there remained a dark green residue, consisting of fat and green colouring matter, with a light brown liquid resting above it. This liquid was poured off, filtered, agitated with a quantity of freshly precipitated oxide of copper, and again filtered. The copper in solution was precipitated by sulphuretted hydrogen, and the liquor, which was of a light yellow colour, evaporated in the apparatus before mentioned. The brown syrup thus obtained, after being treated with cold alcohol to remove some decomposed indican, was mixed with twice its volume of ether: other impurities were thus separated, and when clear the solution was evaporated as before. A clear brown syrup was thus obtained, consisting of pure indican.

Pure indican can only be prepared by the rapid evaporation of its solution at the ordinary temperature, for it is decomposed both by heat and by long exposure to the atmosphere, giving rise to new products. On this account the following description of the apparatus employed for that purpose by Dr. Schunck\* may be inserted here.

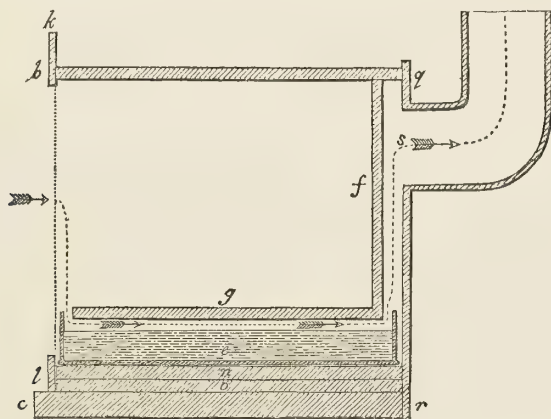


FIG. 8.

---

\* Lit. Phil. Soc., Man., xiv., 182.

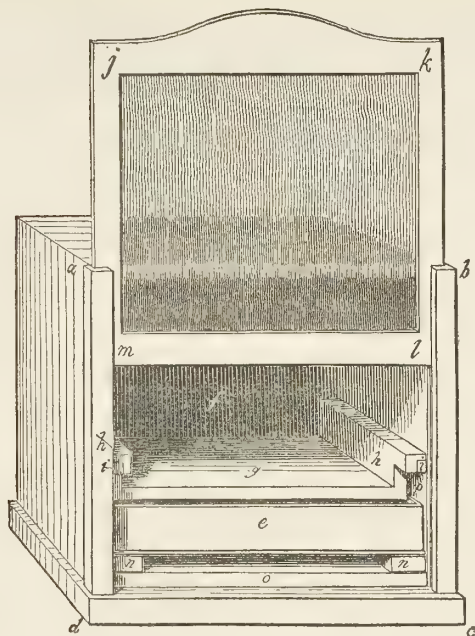


FIG. 9.

"The solution to be evaporated is poured into a dish or  
 "tray of block-tin, about 16 inches square, with per-  
 "pendicular sides 2 inches deep, and capable, therefore,  
 "of containing when full nearly 2 gallons of liquid.  
 "The dish is placed on a shelf fixed at a convenient height  
 "in a wooden box, of which *a, b, c, d*, Fig. 9, represents the  
 "front. This box is closed at the two sides, but open at  
 "the front and back from the shelf upwards. It must be  
 "sufficiently wide to allow the dish to slide easily in and  
 "out, but from front to back it must be so deep as  
 "to leave a space of about half an inch between the  
 "front and the dish. At the distance of about  $1\frac{1}{4}$  inch  
 "from the back of the box, there is fixed in a perpen-  
 "dicular position a board *f*, the upper and side edges of  
 "which are firmly attached to the top and sides of  
 "the box. The lower edge of this board is about on  
 "a level with the upper edge of the tin dish, and is ac-  
 "curately fitted to a shelf *g*, which is suspended by means  
 "of two upright pieces of wood *h, h*,  $2\frac{3}{4}$  inches deep,

“resting on two ledges *i,i*, fixed to the sides of the box.  
“The spaces between *h,h*, and the side walls of the box  
“must be sufficiently wide to allow the sides of the tin dish  
“to move easily up and down in them. By means of sup-  
“ports *n,n*, inserted between the tin dish *e*, and the shelf *o*,  
“the former may be raised so as to bring the surface of the  
“liquid contained in it close to the shelf *g*, which is thus  
“made to hang down within the dish. When the apparatus  
“is to be used, the spaces *p,p*, left between the edges of the  
“dish and the ledges *i,i*, are closed as tightly as possible  
“by means of flat plugs of wood, so as to cause the current  
“of air passing through the apparatus to sweep over the  
“whole surface of the liquid. The front of the box is  
“closed by means of a frame *j,k,l,m*, covered with muslin  
“and sliding up and down in grooves fixed to the sides,  
“which in a great measure prevents the dust which is  
“carried along by the current of air from being conveyed  
“into the liquid. The apparatus is now placed so as to  
“make the back fit as closely as possible to the wall *q,r*,  
“Fig. 8, in which there is an opening *s*, communicating with  
“a steam boiler flue, or the back of the box may be closed  
“with a piece of wood having an opening communicating  
“by means of a pipe with the flue. The section, Fig. 8,  
“shows the direction taken by the air in passing over the  
“surface of the liquid. As the liquid evaporates the dish  
“is raised by means of additional supports, so as again to  
“bring the surface of the former close to the shelf *g*, and  
“thus confine the current within a narrow space. The  
“current of air which I employed, and which was suf-  
“ficiently rapid to cause a constant ripple on the surface of  
“the liquid, was produced by the draught of a steam boiler  
“flue, which carried away the products of combustion from  
“several large fires. I think it probable, however, that the  
“same effect might be produced by causing the whole of the  
“air necessary for the supply of an ordinary stove or close



"fireplace to pass through the apparatus. By means of "the current of air at my disposal I was enabled to evaporate in this apparatus about a pint of water in the course "of twenty-four hours, at a temperature not exceeding "50° F., the temperature of the water being kept by means "of the rapid evaporation rather lower than that of the "atmosphere. The evaporation of a gallon of spirits of "wine by the same means occupied only a few hours."

Prepared as described above, indican is a transparent light brown syrup, from which it is impossible to separate the water which it still retains without decomposing it. Its aqueous solution has a yellow colour, a bitter taste, and a slightly acid reaction. When boiled with caustic alkali it evolves ammonia. The alkaline earths and weak alkaline solutions produce a bright yellow colour with the aqueous solution. Its alcoholic solution gives a bright yellow precipitate with acetate of lead, which is increased by the addition of ammonia; the aqueous solution does not give this reaction.

ACTION OF ACIDS ON INDICAN.—The most important and characteristic property of indican is that when treated with acids it readily splits up into *indigotin*, *indirubin*, and *indiglucin*. If, to an aqueous solution, oxalic or tartaric acid is added, and the mixture allowed to stand, it yields a dark blue or purple precipitate, which is a mixture of indigotin and indirubin. The same decomposition takes place rapidly when an aqueous solution of indican is boiled with a small quantity of sulphuric, hydrochloric, or nitric acid; the liquid first becomes of a sky blue colour, then opalescent, and lastly purple, leaving as the liquid cools a purple deposit of indigotin and indirubin. Both these bodies may be obtained in the crystalline state by sublimation.

If, however, an aqueous solution of indican be boiled or heated for some time in a water bath, it undergoes a change; and if it is now heated with an acid, instead of

yielding the two bodies above described it gives dark brown, almost black, flocks, which when washed, may, by treatment with alcohol, be separated into two bodies, one soluble in that menstruum named *indiretin*, the other insoluble named *indihumin*.

This modified indican is no longer soluble in ether, and only slightly soluble in alcohol, so that on treating the alcoholic solution with ether the unchanged indican remains dissolved, whilst the modified compound is precipitated. This alteration appears to consist in the indican combining with the elements of water under the influence of heat. In the decomposition of the modified indican by acids, indiglucin is formed as in the case of the unmodified one.

Schunck also found leucin in the indiglucin solution. This compound is formed when various animal substances are treated with sulphuric acid, and it also occurs as a product of the putrefaction of cheese. He assigns to indiretin the formula  $C_{18}H_{17}NO_{10}$ , and to indihumin  $C_8H_8NO_5$ . The formula of leucin is  $C_6H_{13}NO_2$ , and of indigotin  $C_{16}H_{10}N_2O_2$ . Although he has analysed indirubin he has not assigned to it any formula.

Schunck has also described two bodies, *indifuscin* and *indifulvin*, which he considers to be directly derived from indican. As they are produced only in very small quantities, and do not give well-defined compounds, it is unnecessary to enter into a minute description of them.

Indigotin, the chief product of the action of acids upon indican, will not be described here, as its great importance as a dyestuff will render it necessary to enter somewhat into detail as to its properties and those of some of its chief derivatives.

Indirubin, the substance obtained from indican along with indigotin, is probably identical with the indigo red of Ber-



zelius, and is formed especially when the decomposition is effected by oxalic or tartaric acid. It is separated from the indigotin by washing with alcohol the flocculent blue precipitate produced in the decomposition; this dissolves the indirubin and leaves the indigotin. On concentrating the alcoholic solution, the indirubin crystallises out in long red needles, which are soluble in alkaline solutions, and which are easily reduced when heated with caustic soda and some deoxidising substance, such as protochloride of tin or grape sugar. On exposing this latter solution to the air it yields purple flakes, which on being collected, washed, dried, and heated between two watch glasses, give a sublimate of beautiful purple needles. These dissolve easily in boiling alcohol, from which they recrystallise on cooling in forms similar to those obtained by sublimation.

Indirubin dissolves completely in cold concentrated sulphuric acid, forming a beautiful purple solution, which on being heated does not blacken, but on the contrary becomes paler and gives off a trace of sulphurous acid. The solution, when diluted with water, yields a fine purple colour to cotton, wool, and silk. It dissolves completely in nitric acid, and the solution, which is at first purple and then red, becomes yellow on boiling. On evaporating this acid solution to dryness, and treating the residue with water, a small quantity of picric acid is dissolved out, leaving a brown resinous substance.

On boiling indirubin with a mixture of sulphuric acid and potassium bichromate it is not decomposed, whilst indigotin is. If it is reduced by means of a mixture of ferrous sulphate with an alkali or other reducing agent, a piece of calico dipped into the solution and then exposed to the atmosphere, becomes dyed of a purple colour and not blue, as would be the case with indigotin. The colour is not removed from fabrics either by acids or soap, and there seems to be little doubt that it is this substance



which gives to well dyed indigo goods that peculiar purple tint which they possess.

*Indiretin* is obtained under the form of a dark brown shining resin, which is transparent only when in very thin layers. When heated, it is decomposed, and gives off strongly smelling fumes, whilst an oil distils over: no crystalline body is formed however. Nitric acid converts it into a mixture of a brown resinous substance, with a little picric acid. It dissolves in ammonia with a brown colour, and the solution gives brown precipitates with the chlorides of barium and calcium. Its alcoholic solution yields with lead acetate a brown precipitate soluble in acetic acid.

*Indihumin* appears to be the indigo brown of Berzelius. It is a sepia brown powder, insoluble in water and alcohol, but soluble in alkaline liquids, forming brown solutions, from which it is reprecipitated by acids in brown flocks. Nitric acid decomposes it easily, forming a yellow solution which on evaporation leaves an orange residue insoluble in water.

*Indiglucin* is prepared by adding to the acid liquor from which the above compounds have been separated an excess of acetate of lead. The sulphate of lead thus produced is removed by filtration, and to the filtrate an excess of ammonia is added, when the indiglucin is precipitated in combination with oxide of lead as a bulky yellow precipitate. This is washed and decomposed by sulphuretted hydrogen. The sulphide of lead is separated, and if the indiglucin solution is not perfectly colourless the last treatment may be repeated, or the solution may be shaken up with animal charcoal. The colourless liquid thus obtained is concentrated to the state of a syrup in the apparatus already described. The syrup is then dissolved in alcohol, and on the addition of twice its volume of ether, the indiglucin is separated as a pale yellow syrup, having a sweetish taste. Mixed with concentrated sulphuric acid

it yields a dark red liquid, which blackens when heated. It is converted into oxalic acid by boiling nitric acid. With cupric sulphate and caustic soda it gives a blue solution, which on boiling becomes yellow, and then gives a deposit of suboxide of copper. By the aid of heat it reduces nitrate of silver and chloride of gold. Acetate and subacetate of lead give no precipitate in its aqueous solution, but one is obtained on the addition of ammonia. On being mixed with milk of lime and filtered, it yields a strong alkaline liquor, which, when boiled becomes quite thick, owing to the separation of a mass of bulky yellow flocks. As the liquid cools, however, these flocks completely redissolve, forming a clear yellow solution. This precipitation and re-solution can be repeated many times.

When an aqueous solution of indiglucin is mixed with yeast and allowed to stand in a warm place, no gas is given off, nor is there any sign of fermentation, but after a few days the liquor is found to have a strongly acid reaction owing to the formation of acetic acid. The two characters last described show that indiglucin is not identical with glucose, but is a peculiar saccharine matter.

Leucin, as before stated, remains in solution with the indiglucin, when indican is decomposed by boiling with acid. The production of this compound from indican is an interesting fact, as the same substance had been discovered long before by Proust, among the products of the putrefaction of gluten and cheese in presence of water. Braconnot had also observed it as a product of the decomposition of gelatin and other animal matters, and Frerichs and Staedeler had found it in animal tissues. Within the last few years it has been prepared synthetically.

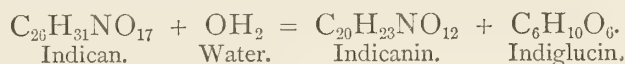
It crystallises from an alcoholic solution in small flat tables, having a pearly lustre, which like the fatty acids are not wetted by cold water. It dissolves readily, however, in boiling water, but is only sparingly soluble in alcohol, and

insoluble in ether. When heated it volatilises without decomposition, producing a sublimate having the appearance of carded cotton. It is soluble in nitric and hydrochloric acids. It gives no precipitate with acetate of lead, neither is one formed on the addition of ammonia, in which respect it differs from indiglucin.

ACTION OF ALKALIS ON INDICAN.—When an aqueous solution of indican is mixed with caustic soda, it becomes of a dark yellow colour, and if it be allowed to stand for several days and then boiled with sulphuric acid, it yields dark flocks, which on being collected and washed are found to contain indirubin, but no indigotin. The indican thus modified by the action of caustic alkali has received from Schunck the name of *indicanin*; it may be prepared by the following method: A solution of indican is mixed with baryta water and left to stand until a portion of it on being boiled with an excess of hydrochloric acid, no longer yields indigotin, but indirubin only. The liquid is then treated with sulphuric acid to precipitate the baryta, and carbonate of lead is added to remove the excess of sulphuric acid. The solution after being filtered is treated with sulphuretted hydrogen and the precipitated sulphide of lead separated. The liquid is now concentrated in Schunck's apparatus, and the dark yellow syrup obtained is treated with alcohol, which dissolves the greater portion. To this solution twice its volume of ether is added to separate any indiglucin that may be present, and the clear liquid is allowed to evaporate spontaneously, when it leaves a yellow transparent glutinous residue which has a bitter taste, and cannot be distinguished in appearance from indican. It is soluble in ether and alcohol. The latter solution yields a bright sulphur-yellow precipitate with acetate of lead, soluble in excess of the reagent when heated, but which reappears on the addition of ammonia. It is decomposed into indirubin and indiglucin, on being



boiled with dilute sulphuric acid. The aqueous solution of indicanin, when boiled with caustic soda, assumes a dark yellow colour, and gives off ammonia. From the following equation it will be seen that indicanin is formed from indican by the taking up of one molecule of water and the loss of one molecule of indiglucin.



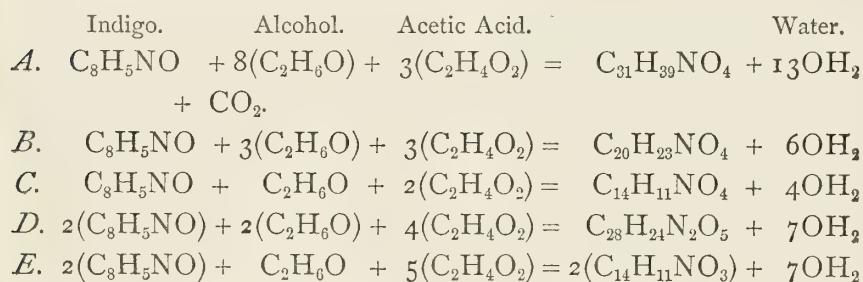
It would seem, therefore, that the action of alkalis on indican is very similar to that of a moderate heat, differing only in the amount of water combined.

The action of alkalis alone on indican having been briefly described, it will be advisable to consider what is the effect produced when alcohol, or alcohol and a reducing agent is present as described by Schunck in his last paper on this subject.\* He states that having almost constantly employed the process of Fritzsche (to which we shall have to refer hereafter) in preparing indigotin, he observed that when he employed but a small quantity of indigo as compared with the quantities of alcohol, grape sugar, and caustic soda, he found that after the indigo had been reduced by the application of heat, instead of reappearing when the liquid was agitated in contact with air, as it does when proper proportions are used, the fluid maintained its yellow colour and no blue indigo appeared. This unforeseen result led him to make a series of experiments, by which he found that the action of caustic soda and grape sugar on the alcohol produced acetic acid, which combined with the alcohol and indigotin to form a compound which did not yield its indigo on being agitated in contact with the air. He found that he could obtain a similar result by substituting acetate of soda for the grape sugar. By these means a dark brown liquid was produced which was mixed with sulphuric acid until it had a slightly acid re-

---

\* Lit. Phil. Soc. Man., xiv., 181.

action, and evaporated to dryness. The residue, after being washed with water to remove the sulphuric acid and sulphate of soda, was found to consist partly of resinous, and partly of pulverulent substances. From this residue Schunck has separated five distinct compounds, all of which are amorphous, and none of them possess characteristic properties; he has, however, ascribed formulæ to them. The substances have not been named, but the following are the equations which show their modes of formation:



These results enabled Schunck to explain some special chemical reactions which occasionally occur in the manufacture of indigo. If the indigo manufacturer does not take the greatest care in conducting the process of fermentation, he will either get an inferior quality of indigo, or a great decrease in the yield of the product, and in some cases even entirely lose the colouring matter. These results take place when the fermentation is either too rapid or too prolonged, the indican in these cases being decomposed into indigotin and indiglucin as usual, but besides this the indiglucin also undergoes a further decomposition into alcohol and acetic acid, which combine with the indigotin to form the mixture of compounds before mentioned, which does not yield its indigo on agitation in contact with the air.

*Oxindicanin.*—When in the preparation of indican the solution has been evaporated in Schunck's apparatus, and is treated with alcohol to dissolve the indican, an insoluble residue is left, to which he has given the name oxindicanin. It is easily purified by solution in a small quantity of

water and precipitation by alcohol. It is a brown glutinous substance, having the appearance of gum. When heated it gives off strongly smelling fumes, and a trace of a crystalline substance sublimes which has a nauseous, but not a bitter taste. When its aqueous solution is mixed with sulphuric acid and boiled, it slowly deposits brown flakes, which have the properties of indifuscin, whilst the liquor contains indiglucin. The formula he assigns to it is  $C_{20}H_{23}NO_{16}$ .

Having noticed indican and the various products obtained from it, which are of scientific interest but of no commercial value, we shall proceed to describe somewhat fully the important colour-giving principle indigotin, already mentioned as one of the products of the decomposition of indican when submitted to the action of acids.

Pure indigotin may be prepared on a small scale by taking two shallow platinum capsules of about 3 inches in diameter, and of such a depth that when placed together with their concave surfaces inwards, they are about  $\frac{3}{8}$  of an inch apart in the centre. In the middle of the lower capsule are placed about 10 grains of coarsely pulverised indigo. On applying a heat of  $300^{\circ}$  or  $400^{\circ}$  F. the indigotin sublimes in beautiful needles of a purple colour and red metallic lustre, which when examined under a microscope are seen to be right rhombic prisms. They have a specific gravity of 1.35, and after being washed with ether or hot alcohol are pure indigotin. These crystals, when heated in the open air, volatilise entirely, giving off beautiful violet vapours resembling those of iodine and having a peculiar odour, but when distilled in a close vessel scarcely any unaltered indigo sublimes, the chief products being aniline, empyreumatic oils, and carbonate and cyanide of ammonium, whilst a bulky carbonaceous mass is left in the retort.

Indigotin is insoluble in water, alcohol, ether, and weak

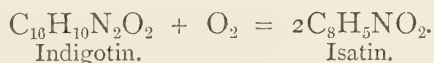


acids and alkalis, but soluble in creosote, phenol, amylic alcohol, chloroform, and bisulphide of carbon. Its best solvents, however, are nitrobenzene and aniline. If finely powdered indigo be boiled with aniline it readily dissolves, forming a blue solution, which if filtered hot, and set aside to cool for some time, deposits almost the whole of the indigo in the crystalline state. After being washed with alcohol and dried, it is chemically pure, having a brilliant coppery lustre, and rivalling in appearance that prepared by sublimation. Boiling paraffin may also be employed for this purpose, the solution having the fine red colour of indigo vapour; in fact, a dilute solution can scarcely be distinguished from an alcoholic solution of magenta. When cold, the indigo crystals, which closely resemble those of sublimed indigotin, may be purified by washing them with benzene. Indigo can also be crystallised from Venice turpentine, and from high boiling point petroleum. Anhydrous acetic acid, to which a drop or two of sulphuric acid has been added, dissolves a sufficient quantity of indigotin to give fast colours when printed on fabrics. If water is added to the solution the indigotin is precipitated unaltered.

Indigotin, under the action of oxidising agents, such as nitric acid, yields three distinct products—isatin, indigotic or nitrosalicylic acid, and picric acid.

*Isatin*  $C_8H_5NO_2$ , was discovered independently by Erdmann and by Laurent in the year 1841. It may be prepared as follows: 1 lb. of indigo is mixed with water so as to produce a thin paste, which is then heated, and nitric acid of specific gravity 1.35 gradually added until the blue colour of the indigo has disappeared: this usually requires 8 to 12 ozs. The product is then diluted with a large quantity of water, boiled, and filtered. On cooling, the impure isatin separates from the filtrate as a brown deposit. To remove a dark coloured semi-fluid resinous body which

adheres to the isatin, it is dissolved in a solution of caustic soda and carefully neutralised with hydrochloric acid. By this means the resin is first precipitated, and on filtering off and adding an excess of acid to the filtrate, the isatin separates in a nearly pure state. After being washed and recrystallised once or twice from hot water it is quite pure. It forms reddish-brown prismatic crystals, belonging to the trimetric system, which are inodorous, and readily soluble in alcohol, but less so in ether. Its formation from indigotin may be thus represented.



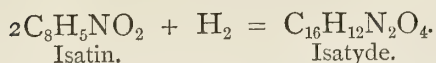
When isatin is heated in a tube, only a small portion sublimes, the greater part being decomposed. When strongly heated in the air, it burns with a brilliant flame, emitting suffocating vapours, and leaving a considerable amount of carbonaceous matter.

Isatin dissolves in caustic potash, forming a purple solution, which becomes yellow when heated, and yields on cooling, *potassium isatate* in the form of small hard prisms.



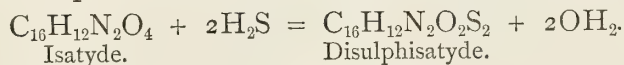
An aqueous solution of isatic acid may be obtained by precipitating the potassium compound with acetate of lead, and after well washing the lead compound, suspending it in water and decomposing it with sulphuretted hydrogen. When the aqueous solution is evaporated in vacuo, *isatic acid* is obtained as a white crystalline powder. If dissolved in water and boiled, this acid splits up into isatin and water.

When isatin is dissolved in water and heated with zinc and a little sulphuric acid, the isatin combines with the nascent hydrogen, and is transformed into a substance called *isatyde*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4$ , which separates as a crystalline powder.



This, if washed and dissolved in hot alcohol, yields microscopic crystals on cooling. Isatyde is insoluble in water, and only very sparingly soluble in boiling alcohol or ether. It dissolves in alkalis with a dark red coloration, which, on the application of heat becomes yellow, potassium isatate and hydrindin potassium being formed. When isatyde is subjected to the action of heat, it turns violet brown.

If, instead of using zinc and sulphuric acid to reduce isatin, sulphuretted hydrogen is employed, the isatyde as soon as it is produced is converted into *disulphisatyde*.



Disulphisatyde is a yellowish-grey tasteless powder, and when treated with a solution of caustic potash, becomes converted into a rose-coloured paste, which after being washed with alcohol and water, consists of a mixture of *indin*,  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}$ , and *sulphisatyde*,  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ . On treating this mixture with a warm concentrated solution of potash, it forms a black solution, which in the course of a few hours becomes a semi-solid mass of black needles of indin potassium,  $\text{C}_{16}\text{H}_9\text{KN}_2\text{O}_2$ . If these are dissolved in boiling absolute alcohol and hydrochloric acid is added, the solution as it cools deposits indin in minute rose-coloured needles. It is insoluble in water, and only very sparingly soluble in alcohol or ether. Nitric acid converts it into *nitrindin*, and when treated with bromine it yields *dibromindin*  $\text{C}_{16}\text{H}_8\text{Br}_2\text{N}_2\text{O}_2$ , as a violet-black powder.

Isatin combines with ammonia, with separation of water giving rise to five well defined compounds.\*

|                   |  |
|-------------------|--|
| Imesatin .....    | $\text{C}_8\text{H}_6\text{N}_2\text{O}$ .         |
| Imasatin .....    | $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3$ . |
| Isamic acid ..... | $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_4$ . |

---

\* Laurent; Ann. Chim. Phys., [3] iii., 483.



Isamide .....  $C_{16}H_{14}N_4O_3$ .

Isatimide .....  $C_{24}H_{17}N_5O_4$ :

In presence of potash or ammonia, sulphurous acid combines with isatin to form a class of compounds called *isato-sulphites*.

Schützenberger, on heating isatin with hydriodic acid in sealed tubes at  $270^{\circ}$  F., obtained three distinct products—*isato-purpurin*, a red substance, soluble in alcohol and ether; *isato-flavin*, a yellow product, insoluble in ether but soluble in alcohol; and a green compound, insoluble both in ether and in alcohol. If instead of operating as above described, one part of indigotin or isatin be mixed with eighty parts of a cold saturated solution of hydriodic acid, and heated in sealed tubes at  $520^{\circ}$  F., as was done by M. Berthelot in 1868, it is completely decomposed: an octane,  $C_8H_{18}$ , is formed boiling at  $248^{\circ}$  F., whilst the nitrogen is transformed into ammonia and the oxygen into water. At the same time a secondary reaction gives rise to marsh gas and heptane  $C_7H_{16}$ .

Although *indigotic acid* or *nitro-salicylic acid* was first obtained by Fourcroy and Vauquelin, its true composition was ascertained by Dumas. To prepare it from indigo, 2 lbs. of nitric acid, of specific gravity 1.28, is introduced into a tubulated retort, to which 1 lb. of coarsely powdered indigo of good quality is gradually added. Great care is required in conducting this experiment, as the action is very violent; the product, which floats on the surface of the liquid, consisting of a small quantity of indigotic acid mixed with a large quantity of a resinous substance, is treated with water to dissolve the acid, and this solution is returned to the acid liquor in the retort. On concentrating the liquid by distillation and allowing it to cool, indigotic and picric acids crystallise out.

This compound, however, is far more conveniently prepared by the action of nitric acid on salicylic acid,

$C_7H_6O_3$ . This acid may be obtained by the action of fused potash on salicin, or still better from the essence of *Gaultheria procumbens*, or wintergreen, largely imported from America. This essence was proved by Cahours to be a compound ether, methyl salicylate,  $CH_3.C_7H_5O_3$ , which, if heated with caustic potash, is decomposed into methyl alcohol which passes off, and salicylic acid which remains behind as a potassium salt. From this, salicylic acid is separated on the addition of hydrochloric acid, and may be purified by washing it with cold water and subsequently crystallising it from boiling alcohol. By the action of nitric acid it is converted into nitrosalicylic acid or indigotic acid,  $C_7H_5NO_5$ , or  $C_7H_5(NO_2)O_3$ .

Nitrosalicylic acid is only sparingly soluble in cold water, but freely so in boiling water and in alcohol. It is easily fusible, and sublimes unaltered at a somewhat higher temperature. With persalts of iron it gives a red colouration, and with salts of lead a voluminous precipitate of a pale yellow colour.

When indigo is acted on by strong nitric acid the product is different, *picric acid*,  $C_6H_3(NO_2)_3O$ , being obtained. This acid was first noticed by Hausmann in 1798. Liebig gives the following method of obtaining it from indigo:—one part of indigo, broken into small pieces, is very gradually and cautiously added to ten or twelve parts of boiling nitric acid of specific gravity 1.43. The action is very violent, and if too much indigo be added at once, an explosion ensues. When the whole of the indigo has been introduced, more nitric acid is added, and the liquid boiled until no more red fumes are given off. On cooling, semi-transparent yellow crystals separate, which are collected, washed with cold water, and then recrystallised. It is now prepared on a very large scale from phenol, and is extensively used in the dyeing of silk and wool.



It crystallises in long, pale yellow, brilliant, rectangular plates, which are very soluble in alcohol, ether, and benzene, and require about eighty-five parts of cold water for solution. It has an intensely bitter taste, and stains the skin yellow. It has been employed in medicine as a febrifuge, but has the disadvantage that if taken for some little time the skin and the whites of the eyes become yellow. It gives characteristic precipitates with several of the heavy hydrocarbons, such as naphthalene and anthracene. Concentrated sulphuric and nitric acids dissolve it, but it is precipitated again unchanged on dilution. Most of the salts of picric acid are crystalline, and when heated are decomposed with explosion.

Dry chlorine has no action on indigo, either at the ordinary temperature or when heated to  $212^{\circ}$  F., but when water is present it is readily attacked; the blue mass assumes a deep orange colour, and a large quantity of hydrochloric acid is given off. If the orange paste thus obtained is submitted to distillation, white needles are deposited in the neck of the retort, which are a mixture of trichloraniline  $C_6H_4Cl_3N$ , and trichlorophenol  $C_6H_3Cl_3O$ . When these products cease to be given off the mass is left to cool, and the resinous orange-coloured residue is boiled with water. The insoluble part consists of a brown resinous substance, easily soluble in potash, from which it is precipitated on the addition of acetic acid. The aqueous solution contains chlorisatin, dichlorisatin, and chloride of ammonium, the first two of which crystallise out as the liquid cools, whilst the ammonium chloride remains dissolved.

The trichloraniline and the trichlorophenol may be separated by distilling them with an aqueous solution of carbonate of potash, when the trichloraniline passes over with the aqueous vapour, leaving the trichlorophenol in the solution in the form of a potassium compound; on cooling,



this separates in white crystals, which, after being purified by two or three crystallisations, may be decomposed by the addition of an acid. Trichlorophenol forms white flocks, having a very disagreeable odour.

To effect the separation of chlorisatin from dichlorisatin the crystalline mass above referred to is treated with boiling alcohol, which dissolves out the chlorisatin and deposits it again on cooling. By repeated crystallisation from alcohol, the compounds may be completely separated and purified.

*Chlorisatin*,  $C_8H_4ClNO_2$ , forms transparent, orange-yellow, four-sided prisms, which communicate to the skin a disagreeable odour, although they are themselves inodorous. It is almost insoluble in cold, but very soluble in hot water. It requires a heat of over  $320^\circ F.$  to decompose it, and then gives off vapours resembling those of burning indigo. When heated with a solution of potash, it dissolves and behaves in a manner similar to isatin. The liquid which at first is of a dark red colour gradually becomes yellow, and on cooling deposits pale yellow crystals of potassium chlorisatate. Chlorisatic acid, however, cannot be isolated, for when the salt is decomposed by a strong acid it splits up into water and chlorisatin.

*Dichlorisatin*,  $C_8H_3Cl_2NO_2$ , crystallises in needles or plates, having a fine orange-red colour. Its properties are similar to those of the monochlorinated compound, except that it is less soluble in water and in alcohol. By the action of caustic alkali, dichlorisatin is also transformed into a salt. This dichlorisatic acid is more stable than that obtained from chlorisatin, as it can be obtained in the form of a yellow powder, having the formula  $C_8H_4Cl_2NO_3$ . It cannot, however, be dried without decomposition.

When treated with ammonium sulphide, chlorisatin yields a pale yellow crystalline powder, analogous to that obtained by the action of reducing agents on isatin. *Di-*

*chlorisatyde*,  $C_{16}H_{10}N_2Cl_2O_4$ , is only slightly soluble in water, but dissolves in ammonia or other alkaline solutions, communicating to them a red tint. At  $356^{\circ}$  F. it is decomposed into chlorindin,  $C_{16}H_8N_2Cl_2O_2$ , and chlorisatin.

All these compounds can be more easily obtained from isatin than from indigo.

When chlorisatin or dichlorisatin is dissolved in alcohol and a current of chlorine is passed through it, amongst the products formed there is one which contains only carbon, chlorine, and oxygen, the nitrogen and all the hydrogen having been eliminated. This substance, which is called *chloranil* or *perchlorquinone*,  $C_6Cl_4O_2$ , forms pale yellow lustrous scales, insoluble in water and in cold alcohol, and only slightly soluble in boiling alcohol; readily in hot benzene. It is volatile without decomposition, and is not acted on by nitric or concentrated sulphuric acids. The action of a dilute aqueous solution of caustic potash converts it into a dark red salt, potassium chloranilate,  $K_2C_6Cl_2O_4$ . The addition of hydrochloric acid to an aqueous solution of this compound precipitates chloranilic acid in brilliant, bright red scales. They are soluble in pure water with a fine violet colour.

Chloranil is also produced by the action of chlorinating agents, such as potassium chlorate and hydrochloric acid, on phenol, aniline, salicin, and many other benzene derivatives.

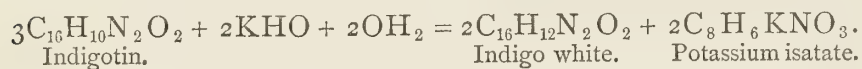
Bromine forms with isatin, compounds analogous to the chlorinated bodies, the formulæ of which are:

|                           |                    |
|---------------------------|--------------------|
| Bromisatin .....          | $C_8H_4BrNO_2$ .   |
| Bromisatinic acid .....   | $C_8H_5BrNO_3$ .   |
| Dibromisatin .....        | $C_8H_3Br_2NO_2$ . |
| Dibromisatinic acid ..... | $C_8H_4Br_2NO_3$ . |

These bodies so closely resemble the corresponding chlorine compounds that it is unnecessary to give a detailed description of them.

The action of alkalis on indigo varies according to the temperature, and the circumstances under which the reaction takes place. In the first stage, Fritzsche states that the potassium compound of a definite acid, chrysanic acid is produced; if an oxidising agent be added, anthranilic acid is obtained, whilst at higher temperatures salicylic acid is formed, and ultimately aniline.

Fritzsche prepares *Chrysanilic acid* by adding finely powdered indigo to a boiling solution of caustic soda of specific gravity 1·45; it dissolves rapidly without giving off any gas, and the liquid assumes a yellowish-red colour. On concentration, yellow crystals make their appearance; and on cooling, the mixture solidifies to a crystalline mass, which, when dissolved in water and exposed to the air, deposits indigo blue; the addition of an acid produces a bulky flocculent brown precipitate, which according to Fritzsche is chrysanilic acid. Gerhardt,\* on the contrary, finds that when indigo blue is heated with potash the following reaction takes place:—



It would appear, therefore, that Fritzsche's chrysanic acid is merely a mixture of indigo white with isatin formed by the action of acids on the potassium isatate, and perhaps, also, products of the further action of potash on this substance.

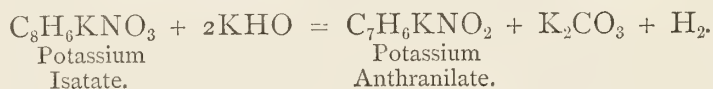
Although the existence of chrysanic acid is more than doubtful, this is not the case with the compound 'called *anthranilic acid*, *phenylcarbamic acid*, or *meta-amidobenzoic acid*, which is a constant and well defined product of the decomposition of indigo under the influence of alkalis. The process for the preparation of this acid is as follows. Indigo blue is kept boiling in caustic potash of specific gravity 1.35, water being added from time to time to

\* Rev. Scient., x., 371.



replace that which evaporates. Previously to the disappearance of the last portions of the indigo, finely pulverised peroxide of manganese is added to the boiling liquid until a sample of it, when diluted with water and allowed to stand, no longer deposits indigo blue. It is then diluted with boiling water, supersaturated with dilute sulphuric acid, and filtered. The filtrate, when neutralised with potash and evaporated to dryness, leaves a residue consisting of a mixture of potassium sulphate and anthranilate, with a brown colouring matter; on treatment with hot alcohol the two last are dissolved out, leaving the potassium sulphate. The spirit is now distilled off, the residue dissolved in water, and a slight excess of acetic acid added, when orange-coloured crystals of impure anthranilic acid are deposited. These may be readily purified by recrystallisation from boiling water with the aid of animal charcoal; on cooling, the hydrated anthranilic acid is deposited in transparent, colourless foliated crystals, with dihedral summits.

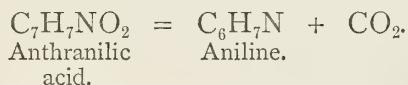
The formation of anthranilic acid from indigo by this process admits of a simple explanation. The action of potash on indigotin, as shown by Gerhardt, converts it into indigo white and potassium isatate; and the addition of manganic peroxide oxidises the white indigo to indigotin again, thus rendering it capable of being converted into potassium isatate. The latter compound is converted into potassium anthranilate thus :



Anthranilic acid has also been synthetically prepared from benzoic acid by converting it first into bromonitrobenzoic acid, then into bromamidobenzoic acid, and finally by the action of sodium amalgam into meta-amidobenzoic or anthranilic acid.

Anthranilic or phenyl-carbamic acid,  $\text{C}_7\text{H}_7\text{NO}_2$ , crystal-

lises in colourless four or six-sided prisms, having a bitter taste. It is only slightly soluble in water, but very soluble in alcohol and ether. Heated at a moderate temperature, it sublimes unchanged, forming white crystals similar to those of benzoic acid; but if mixed with glass and rapidly heated an oily fluid distils over, which is aniline.



Aniline is formed, as before stated, when indigo is mixed with hydrate of potash and distilled. By redistillation pure aniline is obtained equal to about one-fifth of the weight of the indigo taken. Aniline is now prepared on a large scale by the reduction of nitrobenzol by means of iron filings and acetic acid.

The production of picric, salicylic, and anthranilic or phenyl-carbamic acids, and especially of aniline, by the action of chemical agents upon indigo, and the known relation which these bodies bear to phenol and benzene, produced on the minds of chemists a conviction that indigotin in all probability might be prepared synthetically from some member of the benzene series. Recently, Emmerling and Engler\* have succeeded in obtaining indigotin in small quantity from the acetophenone discovered in 1857 by Friedel, and which is obtained by the distillation of a mixture of dried acetate and benzoate of lime. When the acetophenone is acted on by fuming nitric acid, two isomeric nitro-derivatives are formed, one of which is crystalline and the other syrupy; it is the latter which yields the indigotin. For this purpose the syrupy modification of nitroacetophenone,  $\text{C}_8\text{H}_7\text{NO}_3$ , is cautiously heated in porcelain basins until it solidifies on cooling to a tough resinous mass; this is then mixed with nine parts of zinc powder and one part of soda lime, and heated in small portions at

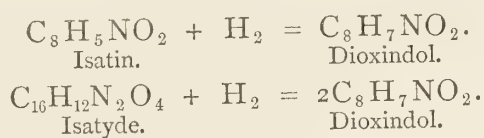
---

\* Deut. Chem. Ges. Ber., iii., 885.

a time in narrow tubes over a Bunsen burner. A dark coloured substance sublimes, which contains indigotin in small quantity. The relation between indigotin and nitroacetophenone is shown by the following equation:—



In the year 1865, Knop\* obtained a body having the formula  $\text{C}_8\text{H}_7\text{NO}_2$ , to which he gave the name of hydrindic acid. This compound, which is also called *dioxindol*, is formed from isatin or isatyde by the action of sodium amalgam in the presence of water; the reactions being as follows:—



Sodium amalgam is added to isatin suspended in water until the liquid becomes of a deep yellow colour, and no longer gives a precipitate of isatin on the addition of hydrochloric acid. On concentrating and allowing it to stand, crystals of sodium dioxindol are obtained, which are dissolved in water, acidulated with hydrochloric acid, and chloride of barium added. The barium dioxindol thus obtained is washed and put to digest in a stoppered bottle with a slight excess of dilute sulphuric acid. Sulphate of baryta is formed, and on evaporating the solution the dioxindol is obtained in yellow needles. These crystallise from hot alcohol in opaque, white, rhomboidal prisms, soluble in both cold and hot water. At  $270^\circ\text{F}$ . it fuses and begins to decompose, and at  $380^\circ\text{F}$ . the liquid assumes a purple colour and aniline is given off. Its colourless aqueous solution, on exposure to the atmosphere, becomes first pink and then red, and is found to contain isatin and indin. It yields easily crystallisable compounds with

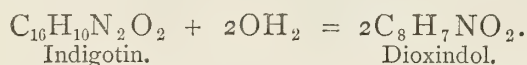
---

\* Jour. pr. Chem., xcvi., 65.



hydrochloric and sulphuric acids, but is violently attacked by nitric acid. It combines with bases. The silver salt, when heated to 140° F., is decomposed, and yields benzoic aldehyde, the essence of bitter almonds.

It will be seen by a comparison of the formulæ that hydrindic acid or dioxindol differs from indigotin by the elements of water.



It seemed probable that indigotin might be obtained from this compound by the removal of the elements of water, and for that purpose it was heated with anhydrous glycerin. Although the water was removed by this means, indigotin was not produced, but a body possessing quite different properties, although having the same composition. Whilst indigotin is crystalline and insoluble in alcohol or ether, the new isomeric substance is amorphous and soluble both in alcohol and in ether, to which it communicates a violet-red colour.

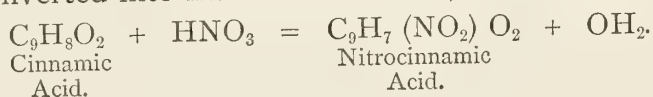
Dioxindol when submitted to the action of reducing agents is transformed into *oxindol*. This change may be effected either by treating it with tin and hydrochloric acid, or which is better, with sodium amalgam in an acid solution. Its formula is  $\text{C}_8\text{H}_7\text{NO}$ . It crystallises in colourless needles, which are very soluble in hot water as well as in alcohol and ether. It combines with bases to form salts; those of potash and soda are soluble and crystalline, whilst those of the alkaline earths and metallic oxides are insoluble.

When this compound is heated in a retort with zinc powder, the oxygen is removed, and a substance called *indol* distils over, having the formula  $\text{C}_8\text{H}_7\text{N}$ . This is first treated with dilute hydrochloric acid to remove any aniline which may have been produced in the reaction, and then dissolved in boiling water. When cold the indol crystal-

lises out in brilliant colourless plates, similar in appearance to those of benzoic acid. Indol may also be obtained directly from indigotin by boiling it with tin and hydrochloric acid until it is converted into a yellowish-brown powder, which, after being washed and dried, is mixed with zinc powder and distilled. Indol then passes over. According to Nencki\* and Kükne,† indol is one of the products of the action of the pancreatic juice on fibrin, albumen, &c.

Indol melts at 125° F., and forms a crystalline mass on cooling. It is very volatile, and although it cannot be distilled alone without decomposition, yet it readily passes over when heated in a current of steam. Its odour resembles that of naphthylamine. It has weak basic properties, and unites with several of the acids to form salts. It is only slightly soluble in cold, but very soluble in boiling water, and also in alcohol or ether. If, to an aqueous solution of indol an equal bulk of fuming nitric acid be added, previously considerably diluted with water, a bulky red precipitate is produced, which is probably a nitrate of indol. A piece of pinewood dipped into an alcoholic solution of indol mixed with a little hydrochloric acid, acquires a cherry-red colour, which, after a short time, becomes of a dirty reddish-brown. These two last reactions of indol are so delicate that the presence of a very small quantity of this substance can be easily detected.

Baeyer and Emmerling‡ have discovered a most interesting process for converting cinnamic acid, an acid obtained from oil of cinnamon, into indol. The cinnamic acid is first converted into nitrocinnamic acid,



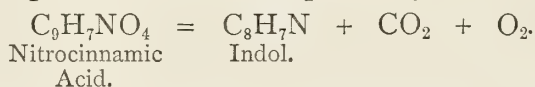

---

\* Deut. Chem. Ges. Ber., vii., 1593.

† Ibid., viii., 206.

‡ Ibid., ii., 679.

which is then mixed with iron turnings and ten times its weight of potassium hydrate, and heated until the potash fuses. When cold the mass is dissolved in water and the solution agitated with ether: this dissolves the indol and a small quantity of aniline which is produced at the same time. On evaporating the ethereal solution, these two bodies are left, and the aniline may be removed by treatment with a little dilute hydrochloric acid. In this reaction the indol is produced from the nitrocinnamic acid by the simultaneous removal of carbonic anhydride and oxygen, by the potash and iron respectively.



Baeyer and Emmerling\* have also recently discovered a method by which isatin can be reconverted into indigotin, one of the most important problems in connection with the chemistry of these compounds. For this purpose isatin is added to about fifty times its weight of a mixture of equal parts of phosphorus trichloride, with chloride of acetyl containing phosphorus in solution, and heated in sealed tubes by means of a water bath to a temperature of about 175° F. The chlorides of phosphorus and acetyl act as solvents for the phosphorus, which removes the oxygen from the isatin. The green fluid produced in this reaction is poured into a large quantity of water, and after being exposed to the air in shallow vessels for twenty-four hours, deposits a blue precipitate. This is a mixture of two colouring matters, one of which is red and soluble in alcohol, which they call *indigo-purpurin*; whilst the other, which is blue and insoluble, presents all the characters of indigotin.

According to Bolley and Crinsoz,† when Bengal indigo is heated between two watch glasses, a small quantity of

\* Deut. Chem. Ges. Ber., iii., 514.

† Technologiste, xxviii., 194.



golden-yellow needles are sublimed before the indigotin. If these are removed they are found to be only slightly soluble either in hot, or in cold water. They are slightly soluble in alcohol, communicating to it a yellowish-green colour. The compound, which contains no nitrogen, is neutral to test paper, and is not acted on by a mixture of sulphuric acid and bichromate of potash.

## CHAPTER VI.

### INDIGO—CONTINUED.

*Indigosulphonic acids.*—There are two commercial preparations obtained by the action of sulphuric acid on indigo, the first of which bears the name of *sulphopurpuric acid*. It may be made by adding one part of good commercial indigo, very finely pulverised, or, better still, purified indigo, to four parts of highly concentrated sulphuric acid, and heating the mixture for a short time, varying from half an hour to an hour, or until a small quantity mixed with a large quantity of water gives a deep blue colour. Great care must be bestowed on this part of the operation so as to avoid the formation of another compound called sulphindigotic acid, which will be described presently. The purple mass thus produced, as soon as it is found to be soluble, is thrown into forty or fifty parts of water, when a beautiful purple precipitate is produced. This is collected on a filter and slightly washed with dilute hydrochloric acid so as to remove the various impurities which the indigo employed may have contained, and also any small amount of sulphindigotic acid which may have been produced.

Sulphopurpuric acid communicates a bluish-purple colour to water, in which it is only slightly soluble. When carbonate or acetate of soda is added to this solution purple flocks are precipitated, which are, however, soluble in a large quantity of water. It also gives precipitates with salts of lime, alumina, and iron. It is not acted on at the ordinary temperature by strong caustic alkali.

The aqueous solution of this acid is decolorised by reducing agents, such as zinc, sulphuretted hydrogen, and chloride of tin; it becomes blue again, however, on exposure to the air.

Sulphopurpuric acid is converted into *sulphindigotic acid* when heated with eight or ten parts of sulphuric acid; or the latter may be manufactured directly from indigo, by heating very carefully one part of finely pulverised colouring matter with ten or twelve parts of concentrated commercial sulphuric acid, or, better, with six to seven parts of Nordhausen acid, to a temperature of 120° F. for several hours. The operation is complete when a small sample is found to be entirely soluble in water. The heated mass is then allowed to cool and dissolved in fifty parts of water; the solution should be of a pure blue colour, the more purple it is the more sulphopurpuric acid it contains. After being allowed to stand for some time to allow any impurities that it may contain, and any sulphopurpuric acid which may have been formed, to deposit; a beautiful blue solution is obtained which contains sulphindigotic acid, mixed with small quantities of hyposulphindigotic acid. Excess of strong caustic alkali decomposes sulphindigotic acid, yielding a yellow liquid, but with weak alkalis it combines to form sulphindigotates. These, when solid, are of a beautiful bronze-blue colour, and dissolve freely in water, yielding blue solutions. They are, however, only very slightly soluble in neutral saline solutions, such as sulphate of soda or the chlorides of sodium and potassium, so that if these salts are added to a solution of an alkaline sulphindigotate, the latter is precipitated in blue flakes.

The following table gives the comparative solubility of the principal sulphindigotates:—

|                           |   |
|---------------------------|---|
| Sulphindigotate of potash | } Soluble in one hundred and<br>forty parts of water. |
| Sulphindigotate of soda   |   |
|                           | Slightly more soluble.                                |



|  |   |  |
|--|---|--|
| Sulphindigotate of baryta                          | { | Very slightly soluble in cold,<br>more soluble in hot water. |
| Sulphindigotates of lime,<br>magnesia, and alumina |   | Very soluble.  |
| Sulphindigotate of lead                            |   | Insoluble.   |

Both acid and salts are decolorised by reducing agents.

A third sulphonic acid exists, called *hyposulphindigotic acid*, which is always formed to a certain extent in the preparation of sulphindigotic acid; it is not, however, of any commercial importance. To separate the two acids and obtain them in a pure state, a piece of flannel which has been thoroughly washed first with soap and carbonate of soda, and then with pure water, is digested in a solution of the ordinary sulphindigotic acid until all the colouring matter is taken up. The dyed flannel is then well washed to remove the excess of free sulphuric acid, after which it is treated with a weak solution of carbonate of ammonia in order to dissolve the acids off the flannel. The blue solution thus obtained is evaporated to dryness at a temperature of 120° F., and the residue treated with alcohol of specific gravity 0.83, which dissolves the hyposulphindigotate of ammonia and leaves the sulphindigotate.

All three acids can be obtained in a state of purity by precipitating the solutions of their respective alkaline salts with acetate of lead, and decomposing the insoluble lead compounds, after they have been carefully washed, by a current of sulphuretted hydrogen: sulphide of lead is formed and a colourless fluid remains, which, when evaporated in contact with the air becomes blue, and leaves an amorphous residue. The acids, which when dry have a slightly astringent acid taste, are very soluble in water and alcohol. The formula of sulphopurpuric acid is  $C_{16}H_9N_2O_2 \cdot HSO_3$ , and that of sulphindigotic acid  $C_8H_4NO \cdot HSO_3$ .

The sulphindigotic acid of commerce known as 'Saxony blue,' is chiefly used by woollen dyers, who add to the dye-beck a little alum and cream of tartar, which helps to fix the indigo on the wool. The green colouring matter which it generally contains is not objectionable in this instance, as it has no affinity for woollen fibre; for dyeing silk, however, the green matter must be removed. This is effected by converting the acid into an impure sulphindigotate of soda, which is known in commerce as indigo carmine. It may be prepared as follows: 1 lb. of very finely pulverised indigo of the best quality\* (or, better still, refined indigo), sieved and carefully dried at a temperature of 150° to 160° F. is put into an earthenware vessel placed in cold water to prevent any rise of temperature. To it, 6 lbs. of sulphuric acid of specific gravity 1.845 is carefully and gradually added, the mixture being kept well stirred during the whole time. The mass is then put in a closed vessel and removed to a stove, where it is kept at a moderate temperature for several days, after which it is dissolved in 5 gallons of water, and a saturated solution of common salt added until the whole of the blue colouring matter is precipitated. The supernatant liquor, which has a dark green colour, is drawn off, and the precipitate is then thrown on a woollen filter and washed with water until the liquid which passes through has a slightly blue tint. By this means an ordinary quality of carmine is prepared, but if a first class quality is required, perfectly free from green colouring matter, it is necessary to operate as follows: The carmine prepared in the manner described is dissolved in a mixture of 5 gallons of water and 1 lb. of sulphuric acid; the sulphuric acid is then carefully neutralised with carbonate of soda, and the whole of the carmine precipi-

---

\* To obtain the indigo in a sufficiently minute state of division it is introduced into a cylinder along with some cast iron shot, and the cylinder is then caused to revolve rapidly.

tated by a solution of salt. The precipitate, after being thrown on a filter and drained, is again dissolved and reprecipitated, this operation being repeated until the green matter is entirely removed, which may be known by the supernatant liquid no longer having a green tint. It is then washed with water until the liquid comes through blue, when it is drained as far as possible, and finally submitted to slight pressure in linen bags: it is now ready for the market. To ascertain if the green colouring matter is removed, a small quantity of the carmine is rubbed on a piece of glazed paper. When the colour dries, it gives a shade varying from a pale blue to a rich coppery purple, according to the mode of manufacture employed; and if any green colouring matter be left it will show itself as a green ring round the blue circle. One pound of indigo yields ten pounds of good carmine.

Another process for the preparation of indigo carmine has been patented by Messrs. L. and E. Bailey, by which it is stated a fine purple carmine can be obtained. They fuse fifteen parts of dry bisulphate of soda in an iron pot, and add to it one part of good indigo, in small quantities at a time, taking care to constantly stir the mass, which swells considerably. The application of heat is continued until a small quantity taken out is found to be entirely soluble in water; the fused mass is then allowed to cool, dissolved in seventy or eighty parts of water, and two parts of common salt are added for every part of the mixture, to precipitate the carmine. It is finally washed with a weak solution of common salt and dried. Bailey's blue forms purple crystalline masses, which give a very bright violet-blue solution. It is soluble in hot concentrated acetic acid, from which it is deposited on cooling in brilliant coppery crystals.

The three following analyses will show the composition of these carmines:—



|                       | Best.             | 2nd quality.      | 3rd quality.       |
|-----------------------|-------------------|-------------------|--------------------|
| Colouring matter..... | 12'4              | 10'2              | 4'96               |
| Saline residue .....  | 13'9              | 4'8               | 5'70               |
| Water .....           | 73'7              | 85'0              | 89'34              |
|                       | <hr/> 100'0 <hr/> | <hr/> 100'0 <hr/> | <hr/> 100'00 <hr/> |

To ascertain the value of any of these sulpho compounds of indigo, a given weight is dissolved in water, a little cream of tartar and alum added, and the colour removed by dyeing wool. The value of the sample is in proportion to the weight of wool dyed and the intensity of shade produced.

Berzelius has studied some of the modifications which the sulphonic acids of indigo undergo when subjected to the action of alkalis and alkaline earths, and his results show that they yield under such influence, yellow, red, green, and violet compounds, which have the power of dyeing wool without a mordant. This illustrious chemist found that when a solution of barium hyposulphindigotate is evaporated in a water bath it leaves a green residue, which is very soluble in water and alcohol, and gives a greenish-grey precipitate with subacetate of lead. When this lead compound is decomposed by sulphuretted hydrogen, it yields a solution of *sulphoviridic acid*, which is green by reflected light and dark red by transmitted light.

When potassium sulphindigotate is mixed with lime water, and gently heated in an open vessel, it becomes red and afterwards yellow. If, as soon as the liquid has become red, the excess of lime be removed by means of a current of carbonic acid, and the clear solution evaporated, a brown residue is obtained, which, when treated with alcohol of specific gravity .82, yields a yellow extract and an insoluble residue. The alcoholic solution is now precipitated with acetate of lead, and the insoluble lead compound, after being washed, is suspended in water and de-

composed by sulphuretted hydrogen; the solution, when filtered from the lead sulphide and carefully evaporated, leaves a crystalline compound, to which Berzelius gave the name of *sulphoflavic acid*. If the residue insoluble in alcohol, is dissolved in water, precipitated by a salt of lead, and the precipitate decomposed by sulphuretted hydrogen, a solution is obtained which on evaporation yields a red amorphous compound, *sulphorufic acid*.

If thirty parts of lime water be heated with one part of potassium sulphindigotate in a close vessel, it assumes a splendid purple colour, and when precipitated with lead and treated in a manner similar to that just described, a brown amorphous body is obtained, to which Berzelius gave the name *sulphopurpuric acid*.

M. Gros-Renaud has also made a similar series of experiments. One of the results which he obtained deserves notice. On adding caustic soda of specific gravity 1.35 to sodium sulphindigotate, the liquor becomes yellow, and a black precipitate is formed, which is soluble in pure water. The yellow liquor undergoes a gradual change on being kept. If it is saturated with sulphuric acid a few hours after it has been prepared, it gives a blue colouration. If the acid is added after twenty-four hours, the liquid assumes a green tint, which gradually becomes violet; whilst after forty-eight hours it assumes an intense red colour under these circumstances. If this liquid be now partially neutralised with carbonate of soda, it imparts to wool a colour varying from pink to crimson-purple, according to the temperature and concentration of the bath. This product differs in many respects from sulphopurpuric acid. It is far more soluble in water, and on the addition of caustic alkali becomes yellow immediately. Wool dyed with this acid yields a red colour to sulphuric acid, whilst sulphopurpuric acid yields a blue.

If a solution of sulphindigotic acid be left in contact

with caustic soda of specific gravity 1.35 for three days, and it is then supersaturated with concentrated sulphuric acid, it gives a yellow liquid and a yellowish-brown precipitate. The latter, when collected and washed, imparts to wool light or dark yellow shades, according as the precipitate has been more or less washed.

When indigotin is acted on by certain chemical reagents it becomes converted into a colourless substance, which has received the name of *white indigo*. To explain this reaction two theories have been proposed. According to the one, the white indigo is a hydride of the blue; according to the other, the indigo blue is an oxide, and the white indigo a hydrate of a body containing less oxygen than the blue.

The following formulæ illustrate these two hypotheses:

|                    |                            |
|--------------------|----------------------------|
| Indigotin.....     | $C_{16}H_{10}N_2O_2$ .     |
| Indigo white ..... | $C_{16}H_{10}N_2O_2.H_2$ . |
| Indigotin.....     | $C_{16}H_{10}N_2O.O$ .     |
| Indigo white ..... | $C_{16}H_{10}N_2O.OH_2$ .  |

The best process yet devised for the preparation of this white indigo was published by Dumas some years ago: 1 lb. of finely powdered indigo is introduced into a closed vessel with 3 lbs. of ferrous sulphate (green vitriol), 3 lbs. of slaked lime, and about 2 gallons of water; the mixture being shaken up from time to time during two days, and finally allowed to settle. The pale yellow liquor is then syphoned off into bottles filled with carbonic acid, at the bottom of which is some hydrochloric acid deprived of air by boiling. As the alkaline solution is run into the bottle, the hydrochloric acid combines with the lime, and white indigo is precipitated. Care must be taken that the bottles are quite full of liquid. After standing some time the precipitate is thrown on a filter under a bell-jar filled with carbonic acid, washed with cold water, thoroughly deprived of air by ebullition, and then dried in vacuo.



As thus prepared, it is a greyish-white amorphous body, tasteless and inodorous, and having a silky lustre. It is insoluble in water and dilute acids, but soluble in alcohol and ether, and in solutions of the alkalis and alkaline earths. These solutions have a yellow tint, but in contact with the air they gradually become blue owing to the re-formation of indigotin: oxidising agents produce the same effect. When heated out of contact with the air, a small quantity of indigotin sublimes and a carbonaceous mass is left. Concentrated sulphuric acid dissolves it with intense purple colouration, and on the addition of water yields sulphindigotic acid. Its alkaline solutions give bulky white precipitates with salts of magnesia, zinc, alumina, and protoxides of iron, manganese, lead, and tin, whilst with cupric and ferric salts it is immediately converted into indigotin. The precipitate which is produced with protoxide of tin is extensively employed, as will be seen further on, for printing indigo on fabrics. If this tin compound be heated, it yields metallic tin and a sublimate of indigotin. White indigo forms two compounds with lime, one soluble, the other insoluble. According to Löwig, the lead compound deflagrates slightly, leaving metallic lead.

A great variety of substances have the property of reducing indigotin.

1. There are the alkali metals which decompose water, the liberated hydrogen combining with the indigotin, whilst the alkali formed at the same time dissolves the white indigo produced. This result is more easily obtained with the amalgams of the metals than with the metals themselves.

2. Certain metals and metalloids in a boiling alkaline solution also reduce indigotin. Such are zinc, tin, antimony, aluminium, and phosphorous.

3. Certain metallic oxides capable of a higher degree of oxidation.

4. Certain acids susceptible of further oxidation, such as phosphorous acid, hypophosphorous acid, and especially hyposulphurous acid,  $\text{H}_2\text{SO}_2$ . Their action is the same in presence of alkalis.

5. Certain phosphides, arsenides, and sulphides, especially sulphide of arsenic.

6. Certain organic substances in presence of an alkali, such as glucose and gallic acid.

7. Certain fermentations in presence of an alkali, such as the butyric fermentation.

Among the compounds which are used on a practical scale for reducing indigo in the presence of alkalis, are protoxide of iron from the sulphate, protoxide of tin combined with alkali, or protochloride of tin, tersulphide of arsenic, glucose, and certain special fermentations.

A method of preparing an indigo vat which gives very satisfactory results has been recently introduced by Schützenberger and Lalande.\* It depends upon the extraordinary reducing power possessed by the salts of the true hyposulphurous acid,  $\text{H}_2\text{SO}_2$ . Schützenberger,† some years ago, found when zinc was introduced into an aqueous solution of sulphurous acid, that it dissolved without evolution of hydrogen, and the yellow liquid thus produced, contained zinc hyposulphite, possessed remarkable decoloring powers. In the method adopted for applying this reaction to the preparation of an indigo vat, a solution of acid sodium sulphite (bisulphite) of about 30° Baumé is agitated in a closed vessel with granulated zinc for about an hour, after which it is drawn off and mixed with a slight excess of milk of lime so as to precipitate the zinc which is in solution. To the clear liquid, containing sodium and calcium hyposulphites, finely powdered indigo is added, and a sufficient quantity of lime or soda to dissolve the

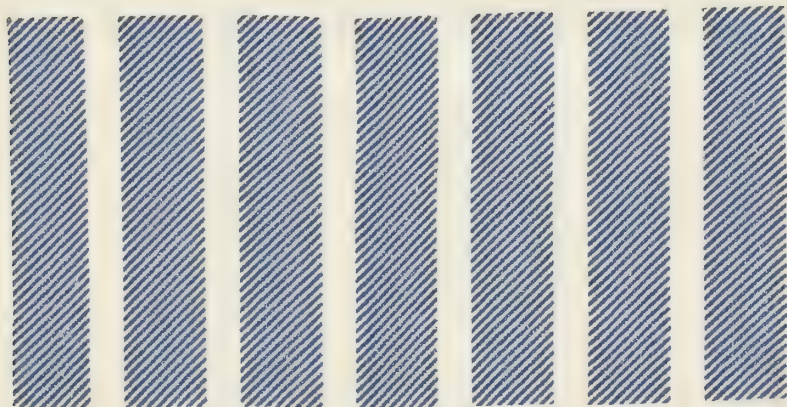
---

\* Chem. Centr., 1873, p. 735.

† Zeits. Chem. [2] v., 545.



white indigo produced by the powerful reducing action of the hyposulphite on the indigotin. As in the ordinary vats, cotton is dyed cold, whilst for woollens the vat should be warm. One pound of indigo to 1 gallon or 1½ gallons of the solution forms a very concentrated vat. A new method of printing, which gives finer shades and sharper definitions than the old one, has been also introduced, employing a concentrated solution of indigo reduced with a large excess of the hyposulphite, and thickened in the usual way. For oxidation the pieces are hung out for twelve or fourteen hours, and then washed and soaped. The annexed specimen was kindly furnished by Messrs. Edmund Potter and Co., of Manchester.



SCHÜTZENBERGER AND LALANDE'S PROCESS.

The printing of reduced indigo is from time to time employed in printworks to produce certain styles of prints. To effect this, protochloride of tin is added to indigo which has been reduced by sulphate of iron in the manner previously explained (p. 182). A white precipitate is thus produced, which is collected and filtered as far as possible out of contact with air; or, a mixture of finely pulverised indigo, caustic soda, and protochloride of tin are heated together until the indigo is reduced, and hydrochloric acid is then cautiously added so as to precipitate the compound of white indigo and tin.



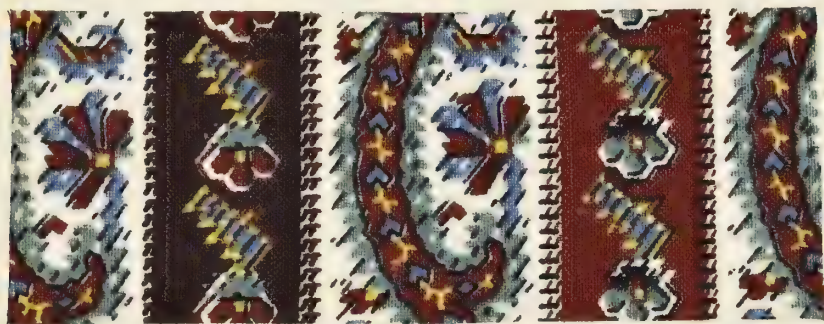
The precipitate is washed, carefully mixed with gum, and printed in the usual manner; but it is necessary to conduct the operations as rapidly as possible, since all the white indigo, transformed into indigotin before penetrating the fibre, is lost to the printer. To facilitate the absorption of the white indigo by the fibre, the goods are passed through milk of lime after being printed; this decomposes the chloride of tin, and the liberated white indigo attached to the fibre gradually changes from a pale green to a blue colour. The pieces are then thoroughly washed, and passed in a weak bath of sulphuric acid to completely fix the indigo in the fabric.

Some years ago, Messrs. Thomas Hoyle and Sons produced some very good specimens of this class of work. Their success was due to an ingenious method of protecting the reduced indigo from the action of the air, by introducing a current of coal gas into the machine, near the printing cylinder. After a little while, however, they gave up its use, owing to the deleterious influence of the coal gas on the health of the workmen.

The chief application of reduced indigo has been for a class of work called chintzes, which require to have fast reds, blues, greens, and yellows. To produce these colours the pieces are first dyed in madder to produce the reds, and the other colours are blocked in. This latter operation is slow and costly, many printers have therefore tried to print the madder mordants at the same time as the reduced indigo and tin. The results generally obtained have been unsatisfactory, as the oxide of tin was but imperfectly removed, and the portion which remained, fixed a certain quantity of alizarin when the pieces were dyed with madder. Owing to this, a dirty purple shade was communicated to the blues and an olive tint to the greens.

The late Mr. J. Lightfoot, of Accrington, overcame this difficulty some time ago, by carefully avoiding any excess of

oxide of tin in the preparation of his reduced indigo compound, for he found by experiment that it was only when the tin was in excess that it injured the colours. According to the specification of his patent, taken out in December, 1867,\* he takes the following proportions:— $1\frac{1}{4}$  lbs. of dry finely powdered indigo, or an equivalent quantity of indigo pulp,  $1\frac{1}{4}$  lbs. of tin crystals, and a gallon of soda or potash ley are boiled together; a gallon of boiling water is then added, and the whole allowed to cool. Eight ounces of sugar, or a pound of treacle are dissolved in 3 gallons of water, and the prepared indigo liquor poured into it. Three quarts of acetic acid, at 8° Twaddle, or  $2\frac{1}{2}$  pints of hydrochloric acid, or 1 pint of sulphuric acid, previously diluted with 1 pint of water, are now added. A precipitate is thrown down, which is a compound of white indigo and protoxide of tin. This is filtered until there is only a gallon left on the filter. To make this pulpy mass ready for printing, it is thickened with 3 or 4 lbs. of gum Senegal or other thickening material, which is stirred in until it is dissolved. He also states that oxide of tin dissolved in alkali, or powdered or granulated tin, may be substituted for the crystals of chloride of tin. The accompanying beautiful specimen, produced by this process, we owe to the kindness of Messrs. F. W. Grafton and Co., of Manchester.



LIGHTFOOT'S PROCESS.

---

\* No. 3,668.



As the fixing of colours by the use of steam is becoming every day more important, the discovery of a good process for the printing of indigo to be fixed by steam would be very valuable, but all attempts to effect this practically have failed up to the present time. M. E. Schlumberger has devised a process which fixes the colour, but is too costly to be carried out practically on a large scale. It consists in mixing together

|   |            |
|---|------------|
| Indigo, very finely ground, with water (twenty parts of indigo to eighty of water)..... | } 4 parts. |
| Fused cyanide of potassium .....  | 4 „        |
| Hydrate of oxide of tin in paste .....  | 4 „        |
| Gum water .....   | 13 „       |

This mixture is printed and steamed. Under the action of steam the cyanide of potassium is decomposed into potash and prussic acid, and the indigo being reduced by the oxide of tin is dissolved by the alkali and becomes fixed on the fabric.

It is important for the printing of indigo, as well as for the preparation of the sulpho compounds previously described, to employ indigo as pure as possible. The following is a brief description of the two processes now commercially employed to prepare what is called refined indigo:—The first process consists in heating indigo with dilute hydrochloric acid, to dissolve the lime and other mineral matters, as well as any starch that it may contain, after which it is well washed and boiled with a weak solution of caustic soda to remove chlorophyll and resinous impurities. It is finally washed, pressed, and dried. The second process was devised by the author, many years ago, for Messrs. Haas and Co., now settled in Leeds, and is founded on the principle of first converting the indigotin of the commercial indigo into white indigo and then reoxidising it in the air. This is effected by placing in a vat one part of finely pulverised indigo, two parts of green copperas



(ferrous sulphate), and two hundred parts of water containing 10 per cent. of caustic soda. Steam is turned in, and the whole kept at the boil for a short time, and then allowed to cool. The clear liquor is run out and exposed in shallow leaden vats to the atmosphere, when the soluble white indigo is oxidised to indigotin, which is precipitated in a nearly pure state.

Having briefly noticed the properties of indigotin and its derivatives, and some of their applications, the next things to be considered are the characters of commercial indigo, and its application in print and dyeworks. The manufacture of this article in Bengal has already been pretty fully described, so that it will merely be necessary to give an outline of the general characters presented by commercial indigos as imported into this country. Although it is very difficult, by any verbal description, to convey a correct idea of the difference in appearance between the many varieties of indigo, yet an attempt may be made to give some notion of the aspect of the different kinds of Bengal indigo, as they are by far the most important, and include all qualities, from the best and finest that come into the market to very ordinary indigo.

When it has not sustained any damage, Bengal indigo is generally imported in the form of large prismatic pieces, packed in cases holding from  $1\frac{1}{2}$  to 2 cwt. The best qualities have a dark violet-blue colour, and take a beautiful coppery lustre on being rubbed with the nail; they produce a sensation of dryness on the tongue; they are easily powdered, and form a fine uniform paste. This kind, however, never contains more than 72 per cent. of pure indigotin, and is characterised by its comparatively low specific gravity, which is but little more than 1.3.

The next qualities are the violet-red indigos of purple hue, with fracture more uniform and lustrous, and they are

heavier and harder. The red shade is caused by the presence of a large quantity of brown and red extractive matter. It is amongst these qualities that the indigos giving the finest colours are found, for it would appear that both the brown and red of the indigo take a certain part in the dyeing process; probably they dissolve and are fixed on the cloth along with the indigo, strengthening the shades. Most dyers prefer these red indigos to the first qualities.

Again, there are qualities of a lighter blue, poorer in colouring matter, but containing also less extractive matter. The impurities consist of mineral matter. They are lighter, do not show the strong coppery lustre of the other two qualities, and produce more strongly the sensation of dryness when touched with the tongue. The worst qualities both of Bengal and all other kinds of indigo, are those which are of a light blue colour, approaching to grey or green. This colour denotes the presence of a large quantity of extractive matter of a different kind to the indigo brown which characterises the red varieties. These indigos are hard, heavy, do not give a coppery reflection, and when touched with the tongue produce very strongly the sensation of dryness.

There are no fewer than forty-three recognised varieties of Bengal indigo, but as it is impossible to enter into a detailed account of each of these in a work like this, an idea of the difference in appearance between the good and bad qualities may be gained from the above short description of the three principal varieties. There have been several methods devised by chemists to determine the relative commercial value of this valuable dye; but before describing them it may be as well to give the following analysis made by Chevreul, which shows the composition of a fair quality of commercial indigo dried at 212° F.

|   |       |
|---|-------|
| Indigotin .....                         | 45    |
| Matters soluble in alcohol .....        | 30    |
| Matters soluble in ether .....          | 12    |
| Resin soluble in hydrochloric acid..... | 6     |
| Mineral matters .....                   | 7     |
|   | <hr/> |
|   | 100   |
|   | <hr/> |

The quantity of hygroscopic water should not exceed 6 per cent. Berzelius found that the portion soluble in alcohol and ether consisted chiefly of four substances, indigo red (indirubin of Schunck), indigo brown (the indihumin of Schunck), gluten, and chlorophyll.

Both organic and inorganic substances are used for the adulteration of indigo. The mineral matters usually added are artificially dyed clay or sand. Starch, Prussian blue, &c., are also employed.

To detect these adulterations 100 grains of indigo, after being dried at 212° F. to ascertain the amount of moisture, is placed in a small earthenware dish and gradually heated to redness. The carbonaceous mass thus formed is taken out, powdered, and again heated until all the carbon is burnt off. The weight of the ash remaining is then ascertained, and should not exceed ten per cent. In a pure indigo, the ash is composed of phosphate and carbonate of lime, potassium sulphate, chloride of potassium, silica, and a small quantity of oxide of iron. To ascertain if starch is present, 100 grains of indigo are pulverised and boiled with very dilute hydrochloric acid; the clear solution yields a beautiful purple colour on adding a few drops of tincture of iodine.

A far more important matter to the consumer, however, is to ascertain the exact amount of colouring matter (indigotin) which a commercial indigo contains. Although the general characters already mentioned as indicating the various qualities of indigo may be sufficient to give the



broker a fair idea of their value, yet, it is always advisable where large quantities are employed, to ascertain by direct analysis their comparative value.

The methods of determining the dyeing power of an indigo can be grouped into four distinct classes.

The first consists of one process only, and was introduced many years ago by a French manufacturer, M. Lubillardière. Ten grains of pure indigotin, and the same weight of the sample to be tested are each carefully dissolved in eight or ten parts of concentrated sulphuric acid, and the solutions made up with water to 1 quart. Equal volumes of these solutions are then placed in graduated tubes, and water is gradually added to the indigotin solution until it has the same intensity of colour as the indigo to be tried. The amount of indigotin present in the latter is in inverse ratio to the amount of water added. Thus if 100 volumes of the indigotin solution requires 138·1 volumes of water to bring it down to the same tint as the other, the proportion will be

$$238\cdot1 : 100 :: 100 : 42.$$

This process is defective, because the colouring power of such a solution is so great, that it requires a large amount of dilution before the liquid is sufficiently transparent for the operator to form a correct judgment of the intensity of shade, and also because some of the other matters in the indigo influence the colour to a certain extent.

The second class is based on the complete oxidation of indigotin. The substances used for this purpose are, bleaching powder, proposed by Chevreul; permanganate of potash, proposed by Lefort; chlorate of potash and hydrochloric acid, proposed by Bolley; and bichromate of potash and sulphuric acid, proposed by Penny. To ascertain the value of an indigo by any of these processes a known weight of the indigo to be tested is finely pulverised, and dissolved in concentrated sulphuric acid. When the solution is com-

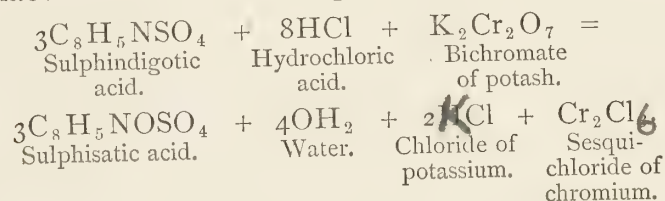
pletely effected, water is added. A solution of pure indigotin, of known strength, is prepared in a similar manner, and by gradually adding to a certain volume of this a solution of the oxidising agent, the amount required to decolorise the solution is readily ascertained. The solution of indigo to be tested is then treated in a similar manner. The quantity of the oxidising solution required in the two operations will be directly proportional to the amount of indigo present.

The details of Penny's method are as follows: 10 grains of the sample of indigo to be tested are finely pulverised, and introduced into a small flask with 120 grains of sulphuric acid of specific gravity 1.845. The flask is then stoppered and placed in a water bath, and the whole is maintained at a temperature of 120° F. for several hours; some broken glass or garnets being added to facilitate the mixture of the indigo and acid when the vessel is shaken. Great care must be taken to ensure the perfect solution of the indigo in the acid. As soon as this is effected, the blue liquid is poured out, and the flask washed out with water; a sufficient quantity being employed to make up the solution to a pint. It is then transferred to a beaker and  $\frac{3}{4}$  of an ounce by measure of strong hydrochloric acid is added. Pure dry bichromate of potash is dissolved in water and made of such strength that an alkalimeter of 1,000 grains contains 7.5 grains of the salt. This solution is added successively, in small quantities, to the dilute sulphate of indigo solution, until a drop of the mixture on being placed on a white slab or on bibulous paper presents a distinct brown or ochrous shade, unmixed with any blue or green. The process is now finished, the number of measures is read off, which gives the per centage of indigotin in the indigo submitted to analysis. It is advisable to keep the indigo solution gently heated while the test liquor is being added: it is also necessary to stir the liquor well after each

addition of the standard solution, and towards the end of the operation to add only a small quantity of the latter at a time. The characteristic change of colour which the mixture undergoes will distinctly indicate the approach of the process towards completion.

The great objection to these modes of determining the amount of indigotin is, that the oxidising agent not only acts on that compound, but also on the other colouring matters described by Berzelius, and the figures obtained are consequently always too high. In fact, whilst commercial indigo usually contains only from 45 to 60 per cent. of indigotin, these processes show from 70 to 80.

The following equation will explain the action which takes place in the bichromate process.

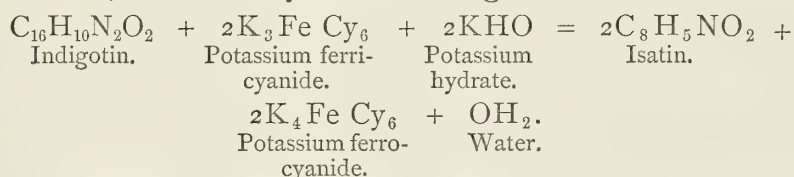


The third class is based on the partial oxidation of indigotin. In this case an alkaline solution is employed instead of an acid one as in the second class.

By the process devised by M. Clement Ullgren, 15 grains of indigotin and of the indigo to be tested are each dissolved in 120 grains of concentrated sulphuric acid. These solutions are made up to a quart with water. One hundred and seventy-five grains of the liquid are diluted to a quart with water, and to this solution carbonate of soda is added, care being taken that there is not a great excess of the alkali. Seventy-five grains of ferricyanide of potassium are dissolved in a quart of water, and a small quantity of caustic soda added. The ferricyanide solution is now very carefully added to the ready prepared weak solutions of indigo, and of indigotin, and the quantity required to convert the blue colour into a pale



yellowish tint, carefully noted. In this case the indigo is oxidised at the expense of the ferricyanide, which is reduced to ferrocyanide; the completion of the operation can therefore be accurately ascertained by testing for the presence of ferricyanide from time to time. The proportion between the quantity required to decolorise the standard indigotin solution, and that of the indigo to be tested, will give the percentage of indigotin in the latter. This process is founded on the conversion of the indigotin into isatin, as shown by the following formula:—



The fourth class is founded on the reduction of indigotin to white indigo and the solution of this latter compound in alkalis, by which it is separated from the impurities it may contain, being afterwards reoxidised by exposure to the atmosphere.

The first of these processes was devised by Fritzsche; 10 or 20 grains of indigo, dried at 212°F., are introduced into a bottle containing an equal weight of grape sugar and three times its weight of caustic soda dissolved in forty parts of alcohol. The quantity of liquid must be such as to quite fill the bottle employed to contain it. It is kept in a warm place until the whole of the indigo is dissolved. The pale yellow liquid is then decanted and exposed to the atmosphere, when the white indigo absorbs oxygen, and the indigotin is deposited often in the form of beautiful prismatic crystals. Schunck has shown, however, (p. 156), that this process may yield very incorrect results; for it is possible that part or even the whole of the indigotin may remain in solution, combined with alcohol and acetic acid; in this state it does not yield a precipitate of indigotin by exposure to the atmosphere.

The second process, devised by the author, although requiring longer time, has been found to give very satisfactory results; by its means a very close approximation is obtained to the amount of colour practically available. Twenty or thirty grains of finely pulverised indigo are placed in a flask, with twice its weight of ferrous sulphate, two hundred of water, and six of caustic soda. The flask is closed by a perforated cork, in which are fixed a small bent tube, which can be connected with a jar of hydrogen, and a syphon going almost to the bottom of the liquid, and closed with a pinchcock. A gentle heat is applied for two hours, after which, the heating is discontinued and the precipitate allowed to settle. The tube is then connected with the jar of hydrogen, and the liquid run off. The residue in the flask is treated again with half the above quantities of iron salt and caustic alkali. The syphoned liquor is placed in shallow vessels and well stirred. The indigotin thus produced is collected, washed, dried, and weighed.

Leuchs\* has introduced a modification of the above process in which the solution of white indigo, instead of being exposed to the air, is acidulated with sulphuric acid, and then oxidised by adding a solution of ammonia iron alum, the reaction being as follows:—



The amount of ferrous salt produced by the deoxidation of the ferric sulphate is ascertained in the usual way, by means of a standard solution of potassium chromate.

The methods followed to obtain fast indigo blues are all based on the principle of the reduction of blue indigo to white indigo. The latter compound is held in solution by an alkali, which enables the dyer or printer to introduce it into the fibre of the cloth, where on exposure to the atmo-

---

\* Zeit. Chem. [2] v. 159.

sphere the alkali combines with carbonic acid, and the white indigo thus liberated absorbs oxygen and becomes insoluble blue indigo. As far as dyeing is concerned the processes can be classed under two heads, hot and cold. The hot process is principally applied to wool, the cold to vegetable fibres, especially cotton.

The oldest and still most generally employed method of preparing cold vats consists in putting into a vat containing about 2,000 gallons of water, 60 lbs. of indigo, in very fine powder, 180 lbs. of slacked lime, and 120 lbs. of ferrous sulphate or green vitriol (free from any trace of copper salt), the two last-named substances being added from time to time. The greater part of the lime employed unites with the sulphuric acid of the iron salt to produce sulphate of lime or gypsum, and the liberated protoxide of iron removes the oxygen from the indigo, becoming converted into ferric oxide, whilst the reduced indigo dissolves in the excess of lime employed. It is always advisable to take the precaution of adding the lime first, and to stir the contents of the vat before adding the copperas, so that there may be excess of lime present to dissolve the indigo as it is reduced. On the other hand, care must be taken that the total amount of lime employed shall not be in great excess, for, as already stated, white indigo forms two compounds with lime, one of which is soluble and the other insoluble; if the latter were formed, it would of course not be available for the purposes of dyeing.

This is not, however, the most serious loss of indigo in the blue-dip vats, the chief being the combination of indigotin with the protoxide of iron, forming a green bulky flocculent precipitate, which, together with the sulphate of lime, is a great source of annoyance to the dyer, increasing the difficulty of obtaining uniformly dyed surfaces.

Many years ago, the author devised the following simple process for recovering the waste indigo:—It consists in



syphoning off the clear liquor which remains in the exhausted or spent vat, and pumping up into a tank the green pulpy mass above referred to, leaving at the bottom of the vat the bulk of the lime and other impurities which may be present. To the pulp in the tank, dilute hydrochloric acid is added to dissolve any carbonate of lime or caustic lime that may be present, and about 10 per cent. of strong hydrochloric acid is then added to decompose the indigotate of lime; the whole being left to settle for twelve hours. The clear liquor is then syphoned off, and a quantity of hydrochloric acid added to the residue until it is strongly acid. By this means the iron compound is decomposed, chloride of iron being produced and white indigo liberated, which rapidly becomes converted into indigotin. After being collected and washed it is ready for use. From 10 to 15 per cent. of indigo is thus recovered. A printer or dyer adopting this method of treating his spent vats can render all the indigotin of the indigo employed available for dyeing, within about 2 or 3 per cent.

It is most important that the indigo used in this and the following dyeing processes should be very finely pulverised in order to facilitate its reduction. Several forms of apparatus are in use for this purpose, but the one most generally employed consists of a vat in which are a pair of millstones, the lower one of which is fixed and the upper one revolves, being driven by means of a lantern wheel. At the bottom of the trough is a tap, by means of which the contents of the vat may be drawn off into a bucket. The indigo is ground with water between the stones, and when it has attained the consistence of cream it is drawn off by the tap into a sieve placed on the bucket. Any portion of the indigo not sufficiently ground is thus retained and put back in the mill.

Messrs. R. Schloesser and Co., of Manchester, have introduced, within the last year or two, a marked improve-

ment in the preparation of cold vats, the invention of which appears to be due to MM. Cohen Frères, of Rouen, and patented by them September 4th, 1867. This process removes the great objections of the bulky precipitate of sulphate of lime, the formation of an oxide of iron, and the loss of indigo by its combination with the oxide of iron just referred to; moreover, as the bath remains much more fluid, the pieces are less apt to be spotted, and a better class of work is produced. The amount of bottoms is only about one-seventh of the bulk of that produced when copperas is employed, consequently the vats can be used a much longer time than in the old process, and there is a saving of time and of indigo. To carry out their process they add to the ordinary 2,000 gallon vat 20 lbs. of ground indigo, 30 lbs. of iron borings, 30 lbs. of powdered zinc, and 35 lbs. of quicklime; the whole is stirred up from time to time for twenty-four hours, when it is ready for use. If the bath is not considered sufficiently strong, a little more lime and zinc are introduced.

The chemical theory of the process is that zinc, in the presence of lime, takes up oxygen from the water, and the liberated hydrogen then converts the indigotin into white indigo, which is dissolved by the excess of lime. In the working of these vats, two difficulties may present themselves; first, the formation of a large quantity of froth on the surface of the liquid; and, secondly, a turbid appearance. Both these effects are due to the presence of an excess of reducing material in the water, and may be easily remedied by stirring up the vat quickly from time to time; this liberates the hydrogen from the frothy mass, and brings up the indigo from the bottom to be acted on by the other agents. The stirring facilitates the clearing of the vat, and renders it soon ready for use.

To dye cotton yarn in these vats, it is simply necessary to dip it for a few minutes in the dye bath and expose it to



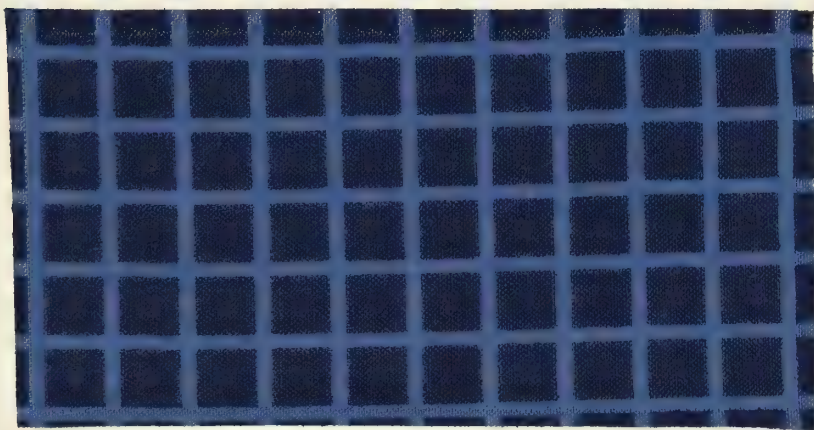
the atmosphere, when the green hue it has acquired passes rapidly into blue. This operation is repeated until the yarn has attained the required depth of shade, when it is passed through dilute sulphuric acid, and after being washed is ready for the market.

To dye calicos the pieces hooked on frames are passed through a bath of weak milk of lime, and then dipped into the reduced indigo vat. After fifteen minutes immersion, the frame is taken out and the cloth exposed to the air for about the same length of time. It is then dipped again, the process being repeated until the required depth of tint is attained. It is finally passed through dilute sulphuric acid and washed. The cold vats are especially used when it is wished to obtain white and yellow designs upon a blue ground. There are two distinct processes by which the whites are produced, one by employing substances to prevent the fixing of the indigo on those places, which is called a 'resist' process; the other, by removing the indigo from them by means of oxidising agents, which is called a 'discharge' process.

To carry out the resist or reserve process 1 lb. of nitrate and 3 lbs. of sulphate of copper are dissolved in a gallon of water. To this are added 4 lbs. of pipeclay, 1 lb. of flour, and 1 lb. of flummery (the refuse product from wheaten starch manufactures). The paste so prepared is printed on those parts of the piece which it is intended should remain white, after which they are hung up in a room for two or three days, according to the style of goods. The pieces are then hooked on to the frames and dipped in the vat, when the indigotin fixes itself on the non-printed parts of the fabric, but will not colour the part where the resist is printed, partly owing to the mechanical resistance of the pipeclay and the insoluble nature of the paste employed, but chiefly to the oxygen of the salts of copper oxidising the indigo before it can penetrate the



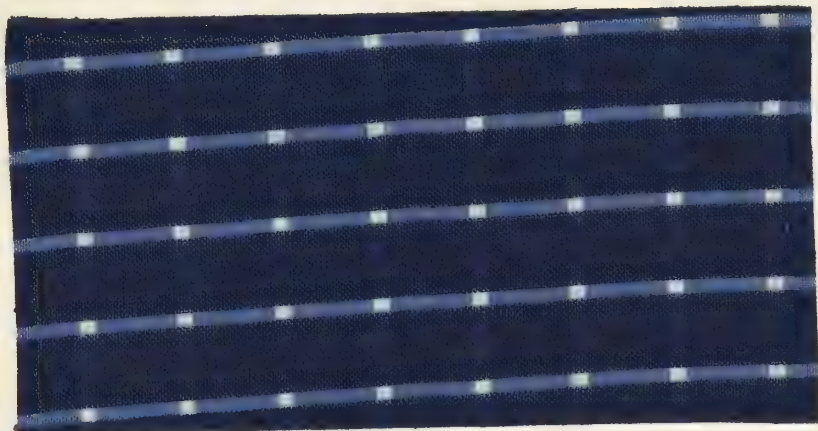
fibre, thus rendering it incapable of fixing itself on the fabric. We are indebted to the kindness of Messrs. Wood and Wright for the two following patterns, illustrating the resist process and the discharge process respectively.



RESIST PROCESS.

The discharge process, first applied by Mr. John Mercer, of Accrington, is carried out as follows:—The cloth, after being dyed with indigo in the usual manner, is padded with a solution of bichromate of potash, containing about 8 oz. of salt to a gallon of water. This operation and the subsequent drying are performed in a dim light, as exposure to a strong light would impair the beauty of the blue, and might even injure the fibre of the cloth. The fabric is now printed with a discharge, containing oxalic, tartaric, citric, and sometimes hydrochloric acid. For roller printing, however, Persoz gives the following process:—In two-thirds of a gallon of water dissolve 2 lbs. of oxalic acid; to the remaining third, add  $7\frac{1}{2}$  lbs. of calcined farina,  $12\frac{1}{2}$  lbs. of sulphate of lead, and 1.28 lbs. of sulphuric acid; then mix the whole. When the cloth has been printed with this discharge it is immediately rinsed in water, containing some chalk in suspension;

then rinsed at the dashwheel, passed through dilute sulphuric acid, and lastly washed in clean water.



RESIST AND DISCHARGE.

When the object in view is to produce a self-colour, a much more rapid process is adopted. Pieces of calico, from which all the sizing material has been removed, are made to pass over a series of rollers *a, b, c, d*, in the vat, A,

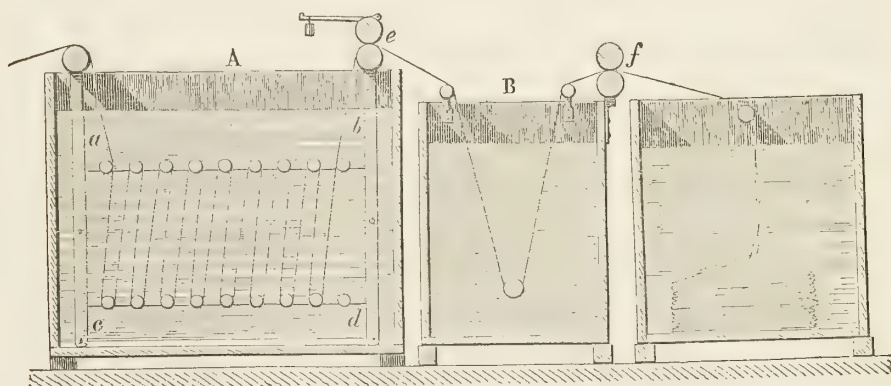


FIG. 10.

Fig. 10, containing reduced indigo, copperas, and caustic soda, which is maintained at a temperature of 150° F.; then through the rollers *e* into another vat, B, containing dilute sulphuric acid, which neutralises the alkali and throws



down the white indigo upon the fabric. They are next carried forward through another pair of rollers, *f*, into a third vat, which must be freely supplied with a current of water; this not only rapidly oxidises the indigo, but removes the sulphate of soda which has been produced. When dried and stiffened the pieces are ready for market.

There is still another process, which is now used only to a limited extent, but was at one time very extensively employed. It produces on the cloth a pale blue, which has a great similarity of tint to that seen on china or porcelain, and from which circumstance it derives its name of *china-blue*. To produce it, the pieces are printed with a mixture containing very finely powdered indigo and a little acetate of iron, and are made to pass through six successive vats. The first two contain lime; the third, sulphate of iron; the fourth, a solution of caustic soda; the fifth, a dilute solution of sulphuric acid; and the sixth, water. When the design has acquired the required depth of blue the pieces are washed, passed once more through weak sulphuric acid, and again washed. The chemical reactions are exactly similar to those in the cold vat process, except that instead of the indigo being in solution it is reduced on the surface of the fabric, and is absorbed by the fibre as quickly as it is rendered soluble.

For dyeing wool, a modification of the old woad vat is employed, but the use of woad being now almost entirely discontinued, indigo has been substituted for woad. It bears the name of the Indian vat, doubtless from the process having been practised in India and imported from thence. It is as follows:—8 lbs. of powdered indigo is added to a bath containing  $3\frac{1}{2}$  lbs. of bran,  $3\frac{1}{2}$  lbs. of madder, and 12 lbs. of potash, which is maintained for several hours at a temperature of 200° F. It is then allowed to cool to 100° F., when fermentation ensues.



After about forty-eight hours the indigo is rendered soluble, being reduced by the decomposition, during the process of fermentation, of the sugar and other products contained in the bran and the madder root. The bath should have a greenish-yellow appearance, and a frothy scum of a blue coppery hue

Of late years, improvements have been made in this class of vats, by which the expense of using madder is avoided. They are now prepared by adding to water, at a temperature of 200° F., 20 buckets of bran, 26 lbs. of soda crystals, 12 lbs. of indigo, and 5 lbs. of slacked lime. After five hours the bath is allowed to cool to 100° F., when fermentation ensues and the indigo is dissolved in the alkali. The management of these vats requires great experience and care, for if the fermentation is too slow the indigo is not properly reduced, whilst if too active large quantities of indigo may be lost. The researches of Schunck, already referred to, not only show the method of avoiding this loss, but explain why it occurs. The remarks previously made as to the causes of failure in the manufacture of indigo are applicable here, namely, that if the fermentation becomes alcoholic and acetic, the non-oxidisable indigo compounds described by Schunck are generated.

While noticing the reduction of indigo by means of organic substances, a process may be described which has been introduced by M. Leuchs,\* of Neuremberg. He employs a new class of reducing agents, namely, pectose, pectin, and pectic acid, which are furnished in abundance by apples, pears, gooseberries, and other fruits; by melons and other *cucurbitaceæ*; but in the largest quantities and at the lowest cost in carrots and turnips. The following is the method he adopts:—Two hundred pounds of soda ley, of specific gravity 1.35, are heated to a temperature of

---

\* Tech., xxvii., 128.

170° F., and 2 lbs. of indigo pulp added. In this alkaline liquor an iron cage is suspended, containing 30 to 40 lbs. of chopped turnips, and the whole raised to the boiling heat. The insoluble pectose of the turnip is thus converted into pectic acid, which is soluble, and the indigo is reduced and dissolved. It is advisable to exclude the air from the boiler as much as possible. When cold, this liquor is added to 42 gallons of water, and is ready for use by the dyer. The inventor considers that his process is more advantageous than the old ones, both for cheapness and convenience. It only requires 9 lbs. of turnips to reduce one of indigo, while all the loss of indigo which occurs in the copperas process is avoided, and the deposit, which is often such a source of annoyance, does not take place. The comparatively short time necessary is a great advantage as compared with the fermentation process, and the goods dyed with it do not require to be passed through an acid bath to fix the indigo and give it brilliancy.

It is a curious fact that indigo is occasionally produced in the human system. Medical men had observed from time to time that urine, secreted under certain pathological conditions, became brown, and sometimes even blue, when exposed to the atmosphere. Hassel discovered that in some instances the colouring matter was indigo, but here again we are indebted to Schunck for much information on the subject. In three papers presented to the Royal Society, he has proved that urine, in cases similar to those examined by Hassel, contained indican. He also observed that indican was a very frequent constituent of urine secreted by persons in a healthy state, and in fact that it is produced generally when persons do not take sufficient exercise; and he has on several occasions succeeded in producing it by taking in his food a rather large excess of sugar.

## CHAPTER VII.

### COCHINEAL, KERMES, GUM-LAC, LAC-DYE, LAC-LAKE, AND MUREXIDE.

COCHINEAL, KERMES, AND LAC-DYE.—These colouring matters are obtained from the animal kingdom, being derived from three distinct species of a peculiar tribe of insects called *Coccina*.

The real cochineal, *Coccus cacti*, lives and propagates on certain varieties of cactus which grow in Mexico, the nopal principally. Kermes, *Coccus ilicis*, is found on a species of oak named the *Ilex*, or *Quercus coccifera*, which grows in Spain, the south of France, Italy, and the islands of the Grecian Archipelago, especially Candia. Poland kermes, *Coccus polonicus radicens*, lives on the roots of the *Scleranthus* of Poland, and the Russian kermes, *Coccus uvaursi* is found in the Ukraine. Lac-dye is prepared from lac, a product derived from the *Coccus lacca*, or *ficus*, which is found in large quantities on the banyan, the juniper, and other trees in India.

The dyes obtained from some species of these insects, were well known to the ancients, and were much used in Persia and India; and although there is no doubt that the Romans were acquainted both with kermes and lac-dye, yet their use seems to have been discontinued in Europe after the fall of that Empire, since no mention is made of it by Giovanni Ventura Rosetti, who, in the year 1429, published the earliest work on dyeing at Venice. On the conquest of Mexico by the Spaniards, they found this dye in



use among the natives, who had employed it for many centuries. It was shortly afterwards introduced into Europe, probably in the year 1518, and owing to the brilliancy and fastness of the colour it soon came into great demand, as would appear from the fact that in 1581 the quantity imported into Spain was 150,000 lbs. From that time this dyestuff was still more largely employed, owing to the discovery of the splendid scarlet which it produces on wool when salts of tin are added to the dye bath. In 1830 it was propagated in the Canary Islands, the island of Teneriffe, Java, and Algiers, and large quantities are now exported from those countries. The best qualities are still obtained from the republic of Honduras.

COCHINEAL.—The cochineal insect belongs to the tribe *Coccina*, several species of which are found in our own country, and these 'bugs' are well known to our gardeners from the injury they do to many plants, especially in hot-houses.

Nothing can be more dissimilar in appearance than the two sexes of these singular insects. The female, from which alone the colour is obtained, forms a mere fleshy mass almost destitute of limbs, remaining attached to one spot on the plant on which it is produced, and from which it continues to derive its nutriment until it attains its full size. The males, on the contrary, are elegant creatures, furnished with a single pair of filmy wings, whilst from the abdomen there grows a pair of long filaments. As already stated it principally lives on a species of cactus called the 'nopal,' or *Cactus opuntia*, or *Cactus coccinilifera*. This plant is indigenous to Mexico, where it grows in the wild state; and from which large quantities of cochineal are collected. It is also extensively cultivated by the native Indians, who often have gardens, or nopaleries containing 60,000 plants. The cochineal obtained from the two sources is of different quality; that from the cultivated plant

is much superior, and is called *mestèque*, or *grana fina*; that collected from the wild plant being called *sylvestra*.

The following is a brief account of the manner in which cochineal is cultivated and prepared for market. In the month of May in the flat lands, and in November in the mountainous districts, the Indians take the stems of the cactus, which they have preserved from a previous crop, and remove from them the young female insects, which are placed on the growing plants, where they multiply with great rapidity. After a period of about three months, the insects are collected in small straw baskets or tin dishes, so formed as to enclose the bottom part of the plant, being swept into it from each stem successively by means of a small brush. They are then destroyed, either by being thrown into hot water, and afterwards dried in the sun or in stoves, which gives the black cochineal, called *zacatilla*; or they are placed in a bag and stoved at once, which leaves upon them that peculiar lustrous appearance which characterises the silver-white cochineal called *blanco*. There is often a second production of cochineal before the wet season sets in; if so, it is scraped off with a knife and dried, but it is of inferior quality, and is sold under the name of *granilla*.

Although a pound of cochineal contains 70,000 insects, an acre of nopal produces about 300 lbs. of cochineal, and there are millions of pounds imported into Europe every year.

If one of the dried insects be placed in warm water for fifteen hours, it swells and takes a hemispherical form, when its structure can be seen. It will be found to be covered with rings, and to be furnished with feet and a rostrum. If the animal is pressed between the fingers thousands of little red granules are exuded, which when placed under the microscope are seen to be the eggs of the insect.

Cochineal has been the subject of several chemical investigations. It was examined by John in 1813, who gives the following as the results of his analysis :—

|   |       |
|---|-------|
| Colouring principle, semi-solid, soluble in water                                   |       |
| and alcohol .....   | 50'0  |
| Gelatin .....   | 10'5  |
| Waxy fat .....  | 10'0  |
| Modified mucus .....  | 14'0  |
| Membrane.....   | 14'0  |
| Alkaline phosphates, and chlorides, and phosphates of lime, iron, and ammonia ..... | 1'5   |
|   | <hr/> |
|   | 100'0 |
|   | <hr/> |

The colouring principle was first carefully examined by Pelletier and Caventou in 1818, who considered it to be an azotised compound. In order to extract the colouring matter they first removed the fatty bodies by means of ether, and then dissolved out the colouring matter by boiling alcohol. On cooling, a red deposit was formed, which was redissolved in alcohol, and the solution shaken up with ether ; a precipitate was thus thrown down, which was the carmine of these chemists, and to which they assigned the formula,



Arppe and Warren de la Rue, however, again investigated the subject in 1847, and came to the conclusion that the colouring matter did not contain nitrogen, although it is accompanied by nitrogenous matter, from which it is very difficult to separate it. They found that it possessed acid properties, and therefore gave it the name of carminic acid. From the results of their analysis they believed it to have the formula  $\text{C}_{14}\text{H}_{14}\text{O}_8$ .

Schützenberger considers that the carmine of Pelletier and Caventou is a compound of carminic acid, and an organic azotised base called tyrosine.

The process devised by Arppe and Warren de la Rue has



been slightly modified by Schützenberger, who succeeded in obtaining the acid in the crystalline form. Cochineal in grains is washed with ether to remove the fatty matters, and then treated several times with boiling water. The addition to the red liquid of a solution of acetate of lead, rendered slightly acid by means of acetic acid, causes a violet-blue precipitate, which contains all the colouring matter; the supernatant liquid being either colourless, or of a faint yellowish tinge. After being thoroughly washed with warm water, the precipitate consists principally of carminate of lead and phosphate of lead, together with a very small quantity of nitrogenous compounds; by far the greater portion of the latter is removed by the washing, and the filtrate on concentration yields small needles of tyrosine, other organic matters remaining in solution in the syrupy liquid.

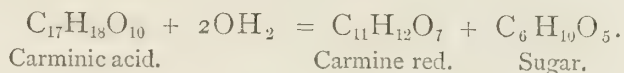
The lead precipitate is suspended in warm water, and a quantity of sulphuric acid added barely sufficient to decompose the carminate, leaving the phosphate unattacked. The carminic acid thus liberated is dissolved in water, and the solution evaporated to dryness in a water bath at a temperature not exceeding 120° F. The residue is dissolved in absolute alcohol, which on evaporation and cooling, yields the carminic acid in the crystalline state. In order to free it from a small quantity of yellow colouring substance, it is dissolved in water, filtered, and evaporated. The residue is then recrystallised from ether, or from absolute alcohol.

According to Schützenberger the formula of carminic acid is  $C_9H_8O_5$ , whilst Schaller makes it  $C_9H_8O_6$ . Hlasiwetz and Grabowski\* published a paper in which they state that carminic acid yields definite compounds with potassium and barium, from an examination of which they find the true formula of carminic acid to be  $C_{17}H_{18}O_{10}$ .

---

\* Ann. Chem. Pharm., cxli., 129.

When boiled with dilute acids it splits up, yielding sugar and a new substance, *carmine red*.



This unfolding of carminic acid into carmine red and sugar is very interesting, as it shows that some animal colouring matters are formed according to the same law as those of the vegetable kingdom, and like them are glucosides. It is not improbable that the tyrosine found in the solutions of cochineal is the product of the decomposition of a peculiar ferment which exists in the insect, but which is destroyed in the stoving, or steeping in boiling water, to which it is subjected in its preparation for the market.

To prepare carmine red, these chemists throw down the colouring matter from a decoction of cochineal in boiling water, by acetate of lead, wash the precipitate carefully, and then decompose the lead compound by dilute sulphuric acid. The dark red solution thus obtained is filtered from the sulphate of lead, and sulphuretted hydrogen is passed through it to precipitate the last traces of lead. The liquid, after being again filtered, is boiled with a little dilute sulphuric acid to decompose the carminic acid, then neutralised by carbonate of baryta, filtered from the barium sulphate, and the colouring matter thrown down by acetate of lead. The precipitate is decomposed by dilute hydrochloric acid, the coloured liquid is filtered, and sulphuretted hydrogen passed through it to precipitate the lead remaining in solution, after which it is evaporated at a gentle heat. The residue is again treated with cold water, which leaves undissolved some resinous flocculent matter and the solution evaporated in vacuo over sulphuric acid. A brilliant purple-red mass is thus obtained, which appears green by reflected light, and when powdered has a dark cinnabar red colour. It is insoluble in ether, but gives beautiful red solutions with water and alcohol.

By fusing carminic acid with caustic potash, these chemists obtained a yellow crystalline substance to which they gave the name *coccinin*,  $C_{14}H_{12}O_5$ . This substance is insoluble in water, but soluble in alcohol and ether. It is very soluble also in dilute alkalis, giving a yellow solution, which, in contact with the air, becomes first green, then violet, and finally reddish-purple.

*Carminic acid* is insoluble in ether, but soluble in water, alcohol, bisulphide of carbon, and benzene. It is not decomposed by a heat of  $280^{\circ}$  F., and may be dissolved without decomposition in concentrated sulphuric or hydrochloric acid. When fixed on fabrics, especially on wool, it is one of the fastest colours known, neither light nor air having any action on it. Nascent hydrogen reduces it, producing a colourless compound, but it is again converted into the red carminic acid on exposure to the atmosphere. Chlorine, bromine, and iodine, however, easily destroy it.

The general properties of the carminates have not been much studied. Schützenberger has, however, obtained a crystallised carminate of soda, to which he assigns the formula,  $Na_2O, C_9H_8O_5$ ; and Messrs. Hlasiwetz and Grabornski have also prepared potassium and barium compounds, having the formula  $C_{17}H_{16}K_2O_{10} + \frac{1}{2}OH_2$ , and  $C_{17}H_{16}BaO_{10}$  respectively. The soda salt crystallises in purple plates.

Guignet\* has recently obtained a lime salt which he prepares by mixing a solution of carminic acid with a salt of lime, the best for this purpose being the bicarbonate. It falls as a black precipitate, which is insoluble in water and alcohol. Concentrated acetic acid dissolves it completely, the solution being of a bright red colour, but on evaporation, the black salt is deposited unchanged. He considers it to be a neutral carminate, but has not analysed it.

Carminic acid gives with caustic alkalis a beautiful red

---

\* Bull. Soc. Chim. [2] xviii., 162.



colour; with baryta and lime waters, a purple precipitate; with salts of barium, and with acetates of lead and copper, purple precipitates; with tin bichloride, a red precipitate; and with cream of tartar, or potassium oxalate, an orange-red precipitate. Alumina removes the whole of the colouring matter from an aqueous solution, yielding a beautiful red lake, which on being heated, becomes first crimson, then purple. The addition to the lake of a little acid, or acetate of alumina, produces the same result.

Warren de la Rue found that by acting on carminic acid with nitric acid of specific gravity 1.4, he obtained a new acid which he called *nitrococcusic acid*, nitrous fumes being given off, and oxalic acid being formed at the same time, the latter no doubt being the product of the decomposition of the sugar already spoken of. The formula of nitrococcusic acid is  $C_8H_5(NO_2)_3O_3 + OH_2$ . It crystallises in fine yellow scales.

Liebermann and Van Dorp confirm these results. They have also obtained a body somewhat similar to coccinin which they call *ruficoccin*, by heating carmine in concentrated sulphuric acid to a temperature of 300° F.

A decoction of cochineal acts rather differently with reagents from a solution of carminic acid, owing to the phosphates and tyrosine which it contains.

The following are its characters:—

|                        |  |
|------------------------|--|
| Acids.                 | { Change the colour to a yellowish-red, causing a slight precipitate.  |
| Alkalis.               | Change it to violet.   |
| Lime water.            | Violet precipitate.  |
| Alum.                  | { Changes its colour to red, then causes a precipitate.                |
| Chloride of aluminium. | { Reddish-violet precipitate, the supernatant liquor becoming crimson. |

|                          |  |
|--------------------------|--|
| Acid chloride of tin.    | { Colour changes to yellow, and<br>a cherry-coloured precipi-<br>tate falls. |
| Neutral chloride of tin. | Violet precipitate.  |
| Bichloride of tin.       | Bright scarlet coloration.   |
| Ferrous sulphate.        | { Violet-grey coloration and<br>precipitate.                                 |
| Acetate of iron.         | { Brown precipitate, which<br>changes to olive-green.                        |
| Sulphate of copper.      | Violet precipitate.  |
| Salts of lead.           | Violet precipitate.  |
| Mercurous acetate.       | Wine-red precipitate.  |
| Mercuric acetate.        | Reddish-brown precipitate.   |
| Sulphate of zinc.        | Dark violet precipitate.   |
| Cream of tartar.         | Red precipitate.   |
| Oxalic acid.             | Red precipitate.   |

As cochineal is an expensive dyestuff, it is liable to be adulterated. One of the most common frauds is practised at Nismes, and other places where perfumery is prepared. The cochineal is put into water for a short time, by which a part of the colour is extracted; it is then dried, and either sold as black cochineal, or placed in a sack and shaken with talc or sulphate of lead, and sold as white cochineal. The latter is easily detected by grinding the cochineal and mixing it with water, when the talc or sulphate of lead falls to the bottom. Good cochineal does not leave above 5 or 6 per cent. of ash.

It is often advisable before buying cochineal to determine its value by ascertaining its comparative tinctorial power, and since it is difficult to prepare carminic acid, the colouring principle of the cochineal, a sample of known good quality must be obtained with which to compare the sample to be tested.

The methods employed are various, but are all based on three principles; the first on a comparison of the depth of

colour of the sample to be tested with that of a similar solution of the standard, the second on the amount of oxidising agent required to destroy the colours in the respective solutions, and the third on their actual dyeing power on equal surfaces of flannel.

In the methods based on a comparison of the strength of colour of the solutions, the colouring matter of the cochineal is extracted by boiling about 15 grains of it in a quart of water, to which is added twenty drops of a saturated solution of alum. After boiling for an hour the liquors are allowed to cool and made up to the original quantity, when they are ready for testing in an apparatus called a colorometer. As, however, several of these have been devised of late years, and the process is equally applicable to many other colours, it has been thought better to leave its description until treating of the general question of the analysis and examination of colouring matters and coloured fabrics.

Among the processes based on the destructive oxidation of the colouring matter, may be mentioned that proposed by Robiquet, who used a standard solution of bleaching powder, and that lately published by Merrick, who employs a dilute standard solution of permanganate of potash. The best, however, of these processes is that adopted by Penny. Twenty grains of cochineal are treated with about 1,000 grains of a dilute potash solution, and this is further diluted with 2,000 grains of water. A solution of red prussiate of potash is then prepared, containing one part of the salt to two hundred of water, and this liquid is added drop by drop from a burette to the cochineal solution until the purple colour is removed, and the liquor has a dull reddish-brown tinge. By a comparison of the quantity of ferricyanide required for the oxidation of the standard cochineal, and that requisite for the sample to be tested, the relative value of the latter is determined.



All these processes, however, are objectionable, as there are in cochineal other organic matters besides carminic acid, which may be oxidised by the reagents employed and thus lead to incorrect results.

To carry out the third principle of testing, which practically is the only thoroughly trustworthy one, the following proportions will be found to give good results :—

For scarlet tints a bath is made composed of—

|                                |            |
|--------------------------------|------------|
| Water .....                    | 1 quart.   |
| Cream of tartar .....          | 32 grains. |
| Oxymuriate of tin .....        | 32 grains. |
| Cochineal, finely ground ..... | 16 grains. |

For crimson tints—

|                       |            |
|-----------------------|------------|
| Water .....           | 1 quart.   |
| Cream of tartar ..... | 12 grains. |
| Alum .....            | 24 grains. |
| Cochineal .....       | 16 grains. |

A piece of flannel weighing 100 grains is then placed in the bath and dyed up to a full tone ; when this has been done, a second piece is put in the bath and allowed to remain until all the colouring matter is exhausted. It is, perhaps, necessary to remark here, that whenever any comparative dyeing experiments are to be made, they ought to be done in the same water bath, so as to be exposed to exactly the same circumstances. If the cochineal to be tested was pure, or merely had part of its colour removed, this dyeing test would give its comparative value, but as occasionally it has been found that cochineal has been adulterated with the colouring matter of Brazil wood, a further test is necessary before its purity can be affirmed. To a solution of the cochineal, lime water in excess is added, when, if pure, all the colouring matter will be thrown down, whilst if any brasilin be present the liquid will have a purple colour.

The chief employment of cochineal is for dyeing silk

and wool by processes similar to that just described for testing cochineal, but unfortunately the brilliant colours so produced are affected by alkalis and soap, which impart to them a purple hue. It is used in calico printing to produce pinks and reds in steam styles. The accompanying sample of cochineal pink has been supplied by Messrs. Wood and Wright.



COCHINEAL PINK, STEAM STYLE.

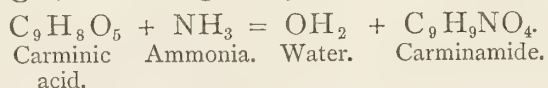
Woollen goods may be dyed, and cotton and silk goods printed also in purple and mauve colours, with a peculiar compound of the colouring matter of cochineal with ammonia, known in the trade as ammoniacal cochineal. This sample has been supplied by Messrs. Z. Heys and Sons, of Barrhead, near Glasgow.



AMMONIACAL COCHINEAL.



AMMONIACAL COCHINEAL.—When one part of ground cochineal is left in contact with three parts of ammonia for several weeks, a chemical action ensues between the carminic acid and the ammonia, the latter losing hydrogen and the former oxygen, so that water is eliminated and an amide is formed, called *carminamide*. According to Schützenberger, the change may be thus represented:—



A solution of carminamide does not give a scarlet precipitate with oxymuriate of tin, like carminic acid, but a beautiful purple one. And the crimson, purple, and mauve colours which it yields, as already stated, are not affected by acids.

There are two commercial preparations of ammoniacal cochineal—one in the state of a thick paste, the other as small flat tablets. The first is prepared by mixing one part of finely powdered cochineal with five or six parts of ammonia: it is left to stand for two or three weeks, and then heated until about two-thirds of the ammonia has been driven off, when it is ready for use.

The second preparation is obtained by adding three parts of ammonia to one of cochineal, in a closed vessel, and leaving them to macerate for a month. After this time, 40 per cent. of alumina in a gelatinous state is added to the mixture, and the whole is then heated in a tinned copper pan until the odour of ammonia can no longer be perceived. The mass when cold should have sufficient consistency to be moulded into cakes.

CARMINE LAKES.—These very beautiful pigments are prepared from a decoction of cochineal, and not from carminic acid, the animal matter which the insect contains appearing to be essential to their production. Their discovery was made accidentally by a Franciscan monk, at Pisa. He had made an extract of cochineal with bitartrate



of potash for medicinal purposes; and one day, putting some acid to the solution, found to his surprise that he had a magnificent red precipitate of carmine. Homberg, in 1656, knew how to obtain it.

Although the modes of preparing the finest qualities of carmine are kept secret by the manufacturers, we know that acid salts, such as bitartrate and binoxalate of potash are usually employed, and the following process will give very satisfactory results:—A pound of cochineal is heated with 2 gallons of water, in which an ounce of alum has been dissolved; it is then raised to the boiling point, and kept at that temperature for three minutes. After having been allowed to settle for a short time, the clear liquid is poured off and put aside for several days, when about an ounce of a bright carmine lake is produced. Cream of tartar may be substituted for the alum employed in this process.

A second process consists in boiling, for two hours, 2 lbs. of powdered cochineal in 15 gallons of water; 3 oz. of pure nitrate of potash are then added, and the boiling continued for three minutes, after which 4 oz. of binoxalate of potash are added, and the liquor again boiled for ten minutes. It is next run off, and when it has become clear, which takes place in about fifteen minutes, it is set aside and allowed to stand for three weeks in shallow glass vessels, when the carmine is deposited. The supernatant liquor covered with fungus is carefully removed, and the carmine collected and dried in the shade.

As these lakes are expensive, they are often adulterated with starch, kaolin, vermilion, &c. The complete solubility of pure carmine lakes in ammonia affords, however, a ready means of detecting these adulterations.

Carmine is generally sold in the state of an impalpable powder, or in small cakes wrapped in fine paper. Gelatinous and albuminous preparations are also made, and are

used by confectioners. Carmine is used principally by artists, paper stainers, and fabric printers.

A lower quality of colour also occurs in commerce called carmine lake or Florentine lake, which was manufactured at Florence for a long time. It is prepared by mixing a weak alkaline solution of cochineal with a solution of alum.

KERMES.—This colouring matter has received its name from the Arabs, the word signifying little worm. It has been known in the East from time immemorial, and according to M. Girardin, Moses mentions it under the name of *jola*. It was also used by both Greek and Roman dyers, being mentioned by Pliny under the name of *coccigranum*. He says that the natives of Hispania paid half their tribute to the Romans with these grains, which were employed for dyeing purple, and that those produced in Sicily were the worst, whilst those from Emerita, in Lusitania, were the best.

In Germany, from the ninth to the fourteenth century, the serfs were bound to deliver to the convents, every year, a certain quantity of kermes among the other products of husbandry. It was collected from the trees on St. John's day, between eleven o'clock and noon, with religious ceremonies, and from this received the name of *Johannisblut*, that is, St. John's blood. At that time a great deal of the German kermes was sent to Venice, to produce the scarlet to which that city give its name.

As already stated, kermes is derived from the *Coccus ilicis*, found on the *Ilex* or *Quercus coccifera*, a shrub which grows on arid rocky soils in hot climates, but which is not specially cultivated for that purpose.

The young female animal fixes itself under the epidermis of the leaves or young shoots of the oak in the early parts of spring. As the insect grows it gradually swells out the epidermis of the leaves or branches, with a multitude of

excrescences somewhat similar to gall-nuts, having a bluish-green hue, and covered with a white powder. During the month of June, or just before the eggs produced would be hatched, the animals are removed, and destroyed by placing them for half an hour in the vapours of acetic acid liberated from heated vinegar; they are then dried. This process gives them the red appearance they usually present when sent into the market as kermes.

When good, kermes is plump, of a deep red colour, having an agreeable odour, and a rough, pungent taste. Its tinctorial matter is soluble in water and alcohol; it becomes yellow or brownish with acids, and violet or crimson with alkalis. Sulphate of iron blackens it, doubtless owing to the presence of a small quantity of tannin derived from the oak on which it lives. With alum it dyes blood-red; with salts of iron, a light purplish-grey; with salts of copper and bitartrate of potash, an olive-green; with chloride of tin and bitartrate of potash, a cinnamon-yellow. Scarlet and crimson dyed with kermes were called grain colours.

Although this colouring matter is seldom used in England, it is extensively employed in the South of France, in Spain, Morocco, and Turkey, to dye Morocco leather, and to give to woollen cloth that particular shade which characterises the cap called 'fez' worn by the Asiatics.

If the colour is not so brilliant as that of cochineal, it has the advantage of not being changed by soap or dilute alkalis, or by perspiration. It is also employed at Rome, Florence, and Milan, to colour a very favourite beverage known as 'alkermes.'

The colour-giving principle of this insect is apparently identical with that of cochineal, but it requires twelve times as much kermes as cochineal to produce a scarlet of the same intensity with a salt of tin.

The kermes of Poland and Russia, which are used



exclusively in the countries in which they are found, are employed in a similar manner to that above described.

LAC, LAC-DYE.—Gum-lac is the product of another variety of *Coccina*, which lives especially on the *Ficus religiosa* or banyan tree. It is a resinoid substance, the secretion of which depends on the puncture of the insect, and is made for the purpose of depositing its ova. Besides the banyan tree, the *Rhamnus jujuba*, or juniper, the *Croton lacciferum*, and the *Butea frondosa* which grows in Assam, Siam, Pegu, Bengal, and Malabar, all yield this product. The animals reproduce themselves with such rapidity, and in such numbers, that they entirely cover the surface of the branches of the trees on which they are deposited, forming solid masses, which are often a quarter of an inch thick, and adhering very firmly to the wood. The natives break off these branches just before the time of hatching, and expose them to the sun to kill the insect. These twigs are sold under the name of *stick-lac*. That of Siam is considered the best, that of Assam the next, while that of Bengal in which the resinous coat is thin, scanty, and irregular is the worst.

According to the analysis of Dr. John, stick-lac has the following composition:—

|  |        |
|--|--------|
| An odorous common resin .....                            | 65.83  |
| A resin insoluble in ether .....                         | 16.67  |
| Colouring matter, analogous to that<br>of cochineal..... | } 3.75 |
| Bitter balsamic matter.....                              |        |
| Dim yellow extract .....                                 | .42    |
| Acid of the stick-lac—laccic acid .....                  | .63    |
| Fatty matter, like wax.....                              | 2.50   |
| Skins of the insects and colouring matter                | 2.08   |
| Salts .....  | 1.04   |
| Earths .....   | .62    |
| Loss .....   | 3.96   |
|  | <hr/>  |
|  | 100.00 |
|  | <hr/>  |

Hatchett's analysis yielded :

|                       |       |
|-----------------------|-------|
| Resin .....           | 68.0  |
| Colouring matter..... | 10.0  |
| Wax.....              | 6.0   |
| Gluten .....          | 5.5   |
| Foreign bodies .....  | 6.5   |
| Loss.....             | 4.0   |
|                       | <hr/> |
|                       | 100.0 |
|                       | <hr/> |

Stick-lac is a dark red transparent resin, breaking with a vitreous fracture. It imparts a purple colour to the saliva, and has a bitter, astringent taste. It yields to water only a part of its colouring matter. It is insoluble in fixed and essential oils, but is slightly soluble in alcohol. Borax solution exercises a special solvent power upon it.

Dilute sulphuric or hydrochloric acid dissolves the colouring matter freely, and the solution thus obtained is sometimes used in Europe to produce scarlet shades on woollen goods, to which it yields its colour without the employment of mordants, and the colours so obtained, although not so brilliant as those of cochineal, are less easily affected by perspiration. Alkalis and soap, however, impart to them a purple hue. Stick-lac is still much used in the East, both in the dyeing of woollen goods and Morocco leather. Besides the stick-lac just described, there are two products prepared from it, known in commerce as "seed-lac" and "shell-lac."

Seed-lac is obtained from the stick-lac by removing the resinous concretion from the twigs, reducing it to a coarse powder, and then triturating it with water in a mortar. By this means the greater part of the colouring matter is dissolved, and the granular portion which remains after being dried in the sun constitutes seed-lac.

It contains less colouring matter than stick-lac, and is much less soluble. The results of Hatchett's analysis were:

|                       |       |
|-----------------------|-------|
| Resin .....           | 88.5  |
| Colouring matter..... | 2.5   |
| Wax .....             | 4.5   |
| Gluten .....          | 2.0   |
| Loss.....             | 2.5   |
|                       | <hr/> |
|                       | 100.0 |
|                       | <hr/> |

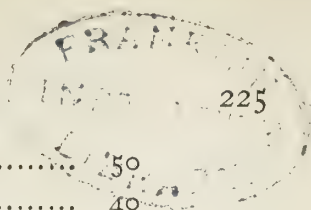
*Shell-lac* is obtained by putting the seed-lac into an oblong bag of cotton cloth, which is held over a charcoal fire until the contents begin to melt, when the bag is twisted so as to strain the liquified resin through its interstices, whence it is allowed to drop upon smooth stems of the banyan tree. In this way the resin spreads into thin plates, in which state it is found in commerce. The Pegu stick-lac being very dark coloured furnishes a shell-lac of a corresponding dark hue, and therefore of inferior value. A stick-lac of an intermediate kind comes from the Mysore country, which yields a brilliant lac-dye and a good shell-lac. According to the analysis of Hatchett it contains :

|                        |       |
|------------------------|-------|
| Resin .....            | 90.9  |
| Colouring matter ..... | .5    |
| Wax.....               | 4.0   |
| Gluten .....           | 2.8   |
| Loss.....              | 1.8   |
|                        | <hr/> |
|                        | 100.0 |
|                        | <hr/> |

*Lac-Dye* and *Lac-Lake* have been imported into this country from India since the year 1796, and are both prepared by acting on stick-lac by a weak alkaline ley. If *lac-lake* is required, this liquor is added to a solution of alum, and the precipitate thus produced is collected, moulded into small lumps about two inches square, and dried. John, who has analysed it, finds it to contain :



# MUREXIDE.



|                        |       |
|------------------------|-------|
| Colouring matter ..... | 50    |
| Resin .....            | 40    |
| Alumina .....          | 9     |
| Foreign matters .....  | 1     |
|                        | <hr/> |
|                        | 100   |
|                        | <hr/> |

The details of the process for preparing *lac-dye* are kept secret, but it appears to be produced by evaporating the above described alkaline solution carefully, in flat dishes, either by artificial heat or by the heat of the sun. It forms cakes about  $2\frac{1}{2}$  inches square, and varying from  $\cdot 5$  to  $\cdot 8$  inches in thickness. It is principally shipped from Calcutta.

These products, especially *lac-dye*, are used in England as substitutes for kermes in the production of scarlets; they require no mordants on woollen cloths, although a little chloride of tin is usually added to prevent the colour assuming a purple hue. From two to three parts of *lac-dye* are equal to one of cochineal.

The tinctorial power of these various dyestuffs may be determined by the same processes as those employed for cochineal.

Some years ago, Messrs. E. Brooke and Co., of Manchester, introduced a *lac-dye* much superior to that imported from India; it is prepared by treating stick-lac with weak ammonia, and adding chloride of tin to this solution, a fine red precipitate is thus formed, which when collected is ready for use.

MUREXIDE.—Although this colour has now been superseded by those derived from coal-tar, it may be noticed here as an example of the great assistance which chemical science has rendered to the art of calico printing.

In the year 1776, the illustrious Swedish chemist, Scheele, discovered in human urine a compound to which he gave the name of uric acid. In 1817, Brugnatelli found that

nitric acid transformed uric acid into a substance which he named erythric acid, but which was subsequently changed to alloxan by Liebig and Wöhler. In 1818, Prout found that this substance, in contact with ammonia, gave a beautiful purple-red colour, which he called purpurate of ammonia, and which is identical with the product known by the name of murexide since the classical researches of Liebig and Wöhler, published in 1837. Thus the matter rested until the year 1851, when Dr. Saac observed that alloxan, although itself a colourless crystallised compound, coloured the skin red when it came in contact with it. This led him to infer that alloxan might be employed to dye woollens red, and further experiments showed that if woollen cloth were prepared with a salt of tin, passed through a solution of alloxan and then submitted to a gentle heat, a most beautiful and delicate pink colour was produced.

In 1856, MM. Deponilly, Lauth, Meister, Petersen, and Albert Schlumberger, applied it as a dyeing material for silk and wool, and obtained red and purple colours, by mixing the murexide with corrosive sublimate, acetate of soda, and acetic acid. For printing on cotton fabrics, a mixture of murexide and nitrate of lead, or acetate of zinc, properly thickened was applied to the cloth. It was then allowed to dry for a day or two, and the colour fixed by passing it through a mixture of corrosive sublimate, acetate of soda, and acetic acid. Very large quantities of printed, coloured, and mixed fabrics were thus produced in 1855 and 1856, but the introduction of the aniline colours, with their superior stability and brilliancy of shade, soon put an end to the use of this colouring matter.

The large quantities of uric acid required to supply the demand for murexide which arose during these years were obtained from Peruvian guano. The guano was first treated repeatedly with hydrochloric acid, and washed until all the soluble matters were removed, leaving an insoluble

mass consisting chiefly of sand and uric acid. Many processes have been devised for converting this crude uric acid into murexide, one of the most simple being to treat it with nitric acid of specific gravity 1.40; when the action was complete, warm water was added to the mass and the whole thrown on a filter. The filtrate, which contained alloxan, alloxantin, and nitrate of urea was evaporated carefully, at a temperature of 175° F., to such a degree, that when left to cool it became a brownish-red, or violet solid, called by its discoverer *carmin de pourpre*; this was the substance used for printing in the manner above described.



## CHAPTER VIII.

### ORCHIL, CUDBEAR, AND LITMUS.

About the year 1300, an Italian named Federigo, who during his travels in the East had observed the tinctorial powers of a certain class of plants of low organisation called *lichens*, introduced the colour into Florence under the name of orchil. For this discovery he was ennobled; moreover, he and his family accumulated a very large fortune, as for many years the whole of the orchil used in Europe was supplied from Florence.

At first the 'weeds,' or lichens used for the production of this colour were collected on the shores of various islands in the Mediterranean, but on the discovery of the Canary Islands in 1402, large quantities were obtained from thence. Later again they were imported from Cape Verd, and now they are also obtained from Madagascar, Zanzibar, Angola, Lima, and various parts of South America.

Lichens are small perennial plants belonging to the class Cryptogamia. They require free access to light and air, and grow either on the stems and leaves of trees, or on rocks, or damp soils. The fructification of the lichens consists of a round or linear, convex or concave cup, called apothecium, or shield, at first closed, but afterwards expanding and producing a disc or nucleus, in which the spores are embedded. The shield is surrounded by a border, which originates either from the substance of the thallus, or from the shield itself, or from both. This class of plants forms the principal flora found in the arctic circle, but the species growing there are not employed to produce

the colouring matter orchil, the varieties used for this purpose being found in warmer, and especially in tropical climates.

The two principal species growing on the shores of the countries already mentioned are the *Roccella tinctoria* and the *Roccella fuciformis*, which are imported and sold as weed of the countries from which they have been brought, as for example, 'Lima weed,' which is the *Roccella fuciformis*, and 'Valparaiso weed,' which is the *Roccella tinctoria*. Of the species growing inland the *Variolaria dealbata*, found on the rocky parts of the Pyrenees, the *Variolaria orcina* of Auvergne, and the *Leconaria tartarea* of Sweden, are the most important.



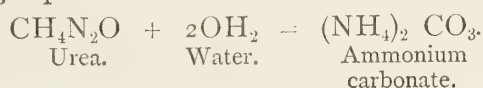
FIG. II.

Lichens do not contain any colouring matters ready formed, but certain colourless compounds, which, under the influence of ammonia and the oxygen of the atmosphere, give rise to orchil. The chief colour-yielding principles existing in these lichens are *erythrin*, *lecanoric acid*, and *evernic acid*.

The manufacture of orchil from lichens was for many centuries conducted in wooden troughs 7 feet long, 3 feet wide, and 9 to 12 inches high, which were closed by wooden lids furnished with hinges. Two hundred parts of the lichens were placed in the trough, together with two hundred and forty parts of decomposed urine, and the mixture well worked every three hours for forty-eight hours. Five parts of slaked lime, one part of arsenious acid, and one-quarter part of alum were then added, and the whole well stirred and allowed to ferment. The stirring was repeated from time to time for a month. The contents of

the trough were then removed into casks and left to stand; the colouring power of the mass being much improved by keeping.

The ammonia necessary for the production of the colouring matter is derived from urea, a substance present in urine, and which under the influence of a special ferment becomes converted into ammonium carbonate, as shown in the following equation :—



The addition of lime then decomposes the ammonium carbonate, with formation of calcium carbonate and liberation of ammonia.

This primitive and offensive process was materially improved soon after the introduction of coal-gas, by substituting the ammoniacal liquor obtained in that manufacture for putrid urine.

M. Freson, a large manufacturer of orchil, in France, found when the weeds were bruised in a mortar with water, and then shaken in a coarse sieve, that a white flocculent matter was separated, which contained nearly the whole of the colouring matter of the lichens.

In order to carry out this process on a large scale, the lichens, after being freed as far as possible from earthy impurities and washed, are ground between millstones with water into a pulp. This pulp is then carefully washed several times with cold water, and the washings thrown on a loosely woven woollen sieve, which retains only the ligneous fibre. To the filtrate a small quantity of bichloride of tin is added, which coagulates the colour-giving principles and determines their precipitation. This deposit is collected, washed, and placed in troughs with the requisite quantity of ammonia. It is stirred from time to time for a month, during which period the colour acquires great intensity, and a beautiful extract is obtained, which can be



used either for printing or for dyeing. As Gauthier de Claubry has pointed out, however, if the lichens are left for any length of time in contact with water, the colouring principle is decomposed and dissolves, so that considerable loss would occur unless the operations are carried on very rapidly.

The following process was communicated to the author by Mr. J. A. Bouck, as the one usually adopted in England:

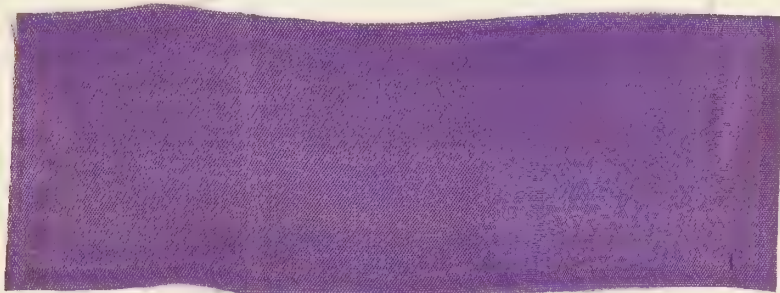
The best orchil is prepared from the *Rocella tinctoria*. The weed is picked by hand or otherwise, torn or cut into small pieces, placed in earthenware mugs or jars, and as much ammonia at 4° Twaddle added as will cover the weed in the jars. The jars are then covered with wooden lids, and kept at a temperature of about 70° F. Fermentation soon commences, and the mass should be turned over and well stirred at least three times daily. The fermentation is allowed to go on until the whole of the colouring matter is extracted from the weed, which generally takes place in fourteen to twenty-one days, if the temperature has been properly attended to. If the fermentation is allowed to go on for too long a time the colouring matter is entirely destroyed, and a dirty brown substance produced.

The mass is taken out of the jars and pressed, and the liquor so obtained is the blue orchil of commerce, and should show 8° Twaddle gravity. The red orchil is obtained by heating the blue orchil at a very low temperature, so as to drive off the ammonia. This operation is best conducted in a double-cased steam pan.

The beautiful purple and mauve colours obtained on silk and wool from orchil are extremely fugitive, losing their brilliancy on exposure to light or to the influence of weak acids, such as sulphurous acid, which is so abundantly produced in our manufacturing districts. M. Marnas, of Lyons, however, succeeded in 1856 in making orchil colours, which gave fast purples and mauves.

In the first instance, as suggested by Dr. Stenhouse, the lichens were treated with milk of lime, but it was afterwards found to be more advantageous to extract them with a dilute solution of ammonia; the colour-giving principle is thrown down from the clear solution by hydrochloric acid, and collected on a filter. This precipitate, after being well washed, is dissolved in caustic ammonia, and the ammoniacal liquor kept at an even temperature of  $153^{\circ}$  to  $160^{\circ}$  F., for twenty to twenty-five days, when the colour-giving principles of the lichens are transformed into a new series of compounds, the most important of which is of a magnificent purple colour. In order to separate this, chloride of calcium is added to the liquid, which precipitates it as a fine purple lake. This, after being washed and dried, is sold under the name of French purple.

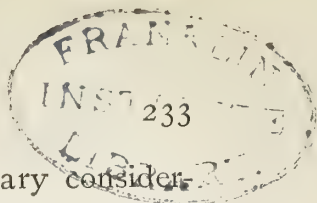
To dye silk or wool with French purple, it is simply necessary to mix the lake with its own weight of oxalic acid, boil with water, and then filter. The oxalate of lime remains on the filter, whilst the colour passes through in solution, and is added to a slightly ammoniacal liquid in the dyebeck; all that is now necessary is to dip the silk or wool in the beck, when it will become dyed a magnificent purple or mauve. In order to dye cotton, it must be mordanted with albumen, or prepared as for Turkey red, before putting it in the bath.



SILK DYED WITH FRENCH PURPLE.



## USES OF ORCHIL.



As the lichens imported into this country vary considerably in the amount of orchil which they yield, it is of the greatest importance to have a simple and accurate method of ascertaining their commercial values. For this purpose Dr. Stenhouse has devised several processes, the following being an outline of the most recent:—100 grains of the lichen are macerated with a solution of caustic soda, containing 5 per cent. of the hydrate, two treatments being sufficient to extract the whole of the colouring principle. A solution of hypochlorite of soda of known strength is then added to the alkaline extract from a graduated alkali-meter, and as soon as it comes in contact with the soda solution of the lichen it produces a blood-red colour. This changes to yellow in the course of a few seconds, when a fresh quantity of bleaching liquid should be poured into the soda solution, and the mixture again stirred. The operation must be repeated as long as the addition of the hypochlorite causes the production of the red colour, care being taken towards the end of the process that only a few drops at a time are added, the mixture being carefully stirred between each addition. By noting how many measures of the bleaching liquor have been required for this purpose, the amount of colouring principle contained in the lichen may be determined.

The employment of orchil is at the present day comparatively limited, but it is still used for producing browns, maroons, and other dark shades in conjunction with other dye-stuffs. Its chief use is to top cheap indigo blues on woollen goods; this is effected by lightly dyeing the fabrics with indigo, which is an expensive dye, and then passing it through a bath of orchil, when it acquires a rich purple hue, similar in appearance to one dyed wholly with indigo.

Robiquet, in 1829, was the first to isolate the peculiar colourless principle, which, when brought in contact with ammonia and oxygen, assumes the fine purple hue of orchil.



This principle he named orcin. He obtained it by treating the *Variolaria dealbata* with strong alcohol, evaporating the solution to an extract, exhausting this with water, and again evaporating to a syrup; on allowing this to stand for some time crystals were deposited having the form of colourless, quadrangular prisms, which are hydrated orcin,  $C_7H_8O_2 + OH_2$ ; orcin is also produced by the decomposition of various compounds obtained from the lichens, such as evernic acid, lecanoric acid, and erythrin. In 1867, Stenhouse published a process by which it may be easily prepared from the latter. Erythrin is dissolved in a slight excess of milk of lime, and boiled for half an hour in a vessel furnished with a long condensing tube, so as to prevent the access of air as far as possible, which otherwise would cause the formation of a red-coloured resinous matter. The solution, containing orcin and erythrite, is filtered, the excess of lime removed by passing a stream of carbonic acid gas through it (or more conveniently on a large scale, by exactly neutralising with dilute sulphuric acid), and then, after concentration, it is evaporated to dryness over a water bath. As orcin is moderately soluble in hot benzene, whilst erythrite and the dark brown colouring matters are insoluble in that menstruum, advantage is taken of this circumstance to effect their separation. The dry mixture of orcin and erythrite above mentioned is boiled with coal-tar oil boiling between  $230^\circ$  and  $300^\circ$  F. (toluene, &c.) in a flask of tin or copper connected with a condenser: a paraffin bath being employed for heating the flask in order to avoid the risk of charring and destroying the erythrite. As the distillation proceeds, the water contained in the mixture of orcin and erythrite distils over with a portion of the coal oil. After twenty or thirty minutes' digestion, the flask is disconnected from the condensing apparatus, and the nearly colourless solution of orcin in coal oil poured out. As soon as it is cool it should

be agitated in a glass flask with about one-tenth of its bulk of water, in order to extract the orcin from the coal oil, which may then be separated from the aqueous solution, poured back into the tin flask, and the digestion continued as before. When this operation has been repeated three or four times, the solid matter in the tin vessel is extracted by boiling water, filtered when cold to separate resinous matters and other impurities, and then evaporated nearly to dryness. After standing several days a large quantity of erythrite crystallises out. This may be purified by washing with cold spirit, pressing, and recrystallising once or twice from hot water, with the addition of some animal charcoal. The aqueous solutions obtained by the above method, on cooling, usually deposit a quantity of nearly colourless crystals of orcin, and the remainder in solution is readily obtained by sufficient concentration. If it is wished to obtain colourless orcin, it is only necessary to purify by a second treatment with benzene, and recrystallisation from water. The advantage of this method consists not only in enabling us to separate orcin and erythrite easily, but also to obtain pure orcin from mixtures contaminated with large quantities of colouring matter. When operating on very large quantities of the mixture, however, it is easier and more advantageous to separate the orcin from the erythrite by crystallisation, as the latter is much more soluble in cold water than the former. Orcin can readily be obtained colourless by distilling it *in vacuo*.

Orcin melts below  $212^{\circ}$  F., losing its water of crystallisation, and becoming anhydrous. Heated with care to  $550^{\circ}$  F. it distils unchanged. It has a sweet, somewhat astringent taste, and is freely soluble in alcohol or ether, and in hot water. When crystallised from ether the crystals are anhydrous. It is neutral to test-paper, but in its chemical constitution, and in many of its reactions, there is a close analogy to phenol. Thus, when in a state



of fusion, it decomposes alkaline carbonates, and it also precipitates silica from alkaline silicates. According to De Luynes, on the other hand, it precipitates several of the alkaloids from their acid solutions.

When dissolved in water or alcohol, it does not give precipitates with bichloride of mercury, sulphate of copper, tannin, gelatin, or acetate of lead. With subacetate of lead it gives a white precipitate, and with persalts of iron a red one. With bleaching powder it gives a purple-red colour, which rapidly changes to a deep yellow. Treated with chlorate of potash and hydrochloric acid, or with hydrate of chlorine, it yields a pentachlorinated compound  $C_7H_3Cl_5O_2$ . With bromine it yields, besides the monobromicin of Lampater,\* two definite products—a pentabromo and a tribromo derivative. With picric acid it gives a beautiful crystalline compound, having the appearance of bichromate of potash; this is soluble in alcohol and ether, but is decomposed by benzene into picric acid and orcin.

When orcin is acted on by cold fuming nitric acid it yields a red-coloured matter, which is precipitated on the addition of water. De Luynes has observed that a red colouring matter is produced when orcin is exposed to the vapour of nitric acid by placing it under a bell-jar along with a vessel containing the concentrated acid. The crystals first become brown, then red, and after a few days the transformation is complete. It differs from the compound obtained on exposing orcin to the action of ammonia and oxygen, for it dyes silk and wool red without a mordant, and yields a purple colour with alkalis, which is changed to red by acids. Although boiling nitric acid converts orcin into oxalic acid, nitro substitution compounds may be obtained by using proper precautions. Stenhouse prepared† *trinitro-orcin*  $C_7H_5(NO_2)_3O_2$ , by dissolving orcin in a small

---

\* Ann. Chem. Pharm., cxxxiv., 258.

† Proc. Roy. Soc., xix., 410.

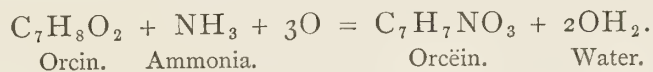


quantity of water, and adding the solution slowly to nitric acid of specific gravity 1.45, previously cooled in a freezing mixture of ice and salt. The pale brown solution thus obtained is then gradually added, with constant stirring, to concentrated sulphuric acid, also cooled by means of a freezing mixture. The temperature during the operations should not at any time be allowed to rise above 14° F.

After twenty minutes the resulting pasty mass is poured into a mixture of crushed ice and water, which precipitates the crude nitro-compound as a yellow or orange-coloured granular powder. After being washed and crystallised from boiling water, it forms large yellow needles, soluble in alcohol, ether, and benzene. It dyes the skin yellow, like picric acid, but is tasteless. It volatilises slightly at 212° F., melts at 290° F., and decomposes with slight explosion immediately afterwards.

Two isomeric *mononitro-orcins*\*  $C_7H_7(NO_2)O_2$  have also been obtained, being produced along with other compounds by the action of a mixture of nitric and nitrous acids on an ethereal solution of orcin. The *α-nitro-orcin* crystallises in long orange-red needles, which melt at 248° F., and are readily soluble in alcohol and ether, whilst *β-nitro-orcin* forms short lemon-yellow needles, which melt at 239° F.

The most important property of orcin, however, in connection with the arts, is that, when moistened and exposed to the atmosphere in presence of ammonia, it becomes converted into a beautiful purple colour. Robiquet, who first observed this reaction, gave to this new substance the name of *orcëin*. Dumas, who further studied the subject, considered the transformation to be



Orcin.      Ammonia.                      Orcëin.                      Water.

De Luynes, who has also examined this remarkable re-

---

\* Weselsky *Deut. Chem. Ges. Ber.*, vii., 439.

action, says that when dry gaseous ammonia and dry orcin are used no coloration takes place, but that when orcin is dissolved in a solution of ammonia and maintained at a temperature of 122° F. for several days, care being taken to replace the ammonia as it evaporates, a highly coloured violet solution is obtained, which, after being filtered and evaporated, leaves a violet residue of orcéin. The insoluble residue on the filter, after being washed with dilute solution of ammonia, is dissolved in boiling alcohol and allowed to cool. A brown deposit is thus obtained, which under the microscope is seen to consist of a multitude of small colourless crystals, more or less contaminated with a brown resinous substance. This crystalline deposit is insoluble in water and ammonia, but is slightly soluble in alcohol, to which it imparts a crimson colour. It yields with alkalis a violet solution, and with sulphuric acid a deep blue. De Luynes also found that orcin under the influence of ammonia can be oxidised by other agents than oxygen. Thus, by boiling a solution of orcin and ammonia with potassium bichromate or permanganate, or with peroxide of barium, these agents were reduced, and orcéin formed. When the ammoniacal solution of orcéin is put under a bell-jar in presence of nitric oxide, the gas is rapidly absorbed, and a colouring matter of great intensity produced.

De Luynes and Lionet have also obtained several orcin derivatives by heating equivalent quantities of crystallised orcin, and of the iodides of the various alcohol radicles. With the iodides of methyl, ethyl, and amyl, they obtained:

|                   |                          |
|-------------------|--------------------------|
| Methylorcin ..... | $C_7H_7(CH_3)O_2$ .      |
| Ethylorcin .....  | $C_7H_7(C_2H_5)O_2$ .    |
| Amylorcin .....   | $C_7H_7(C_5H_{11})O_2$ . |

The first two bodies are liquid and syrupy, the third crystallises in needles.

By heating a mixture of 1 molecule of orcin with 2 molecules of the iodide, and potassium hydrate, they obtained :

Diethylorcin .....  $C_7H_8(C_2H_5)_2O_2$ .

Diamylorcin .....  $C_7H_8(C_5H_{11})_2O_2$ .

These two bodies are syrupy. The first distils unchanged at  $470^\circ$  to  $480^\circ$  F.

Lastly, on adding the iodides and potash in great excess, they state that trimethylorcin,  $C_7H_5(CH_3)_3O_2$ ; triethylorcin,  $C_7H_5(C_2H_5)_3O_2$ ; and triamylorcin,  $C_7H_5(C_5H_{11})_3O_2$  are formed. Trimethylorcin is liquid and distils without alteration at about  $480^\circ$  F., and triethylorcin distils at  $510^\circ$  F.

*Erythrin*.—This compound, one of the most interesting substances existing in the orchil weed, was discovered by Heeran in the *Roccella fuciformis*, and has since been studied by Schunck, Stenhouse, Hesse, and De Luynes.

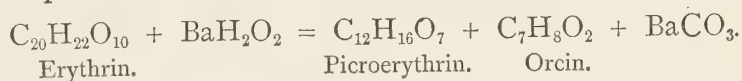
The best process for its extraction is that devised by Stenhouse, which consists in macerating the lichen with lime and water : 3 lbs. of the *Roccella fuciformis* are macerated for twenty minutes with milk of lime, made by slaking  $\frac{1}{2}$  lb. of lime in 3 gallons of water. This maceration is repeated three times. The weaker solutions may be employed with advantage to extract a fresh quantity of the weed. The solution is filtered, and hydrochloric acid added to the filtrate in order to precipitate the erythrin, which is collected on a filter, and washed once or twice with water to remove the chloride of calcium and excess of hydrochloric acid, this is most conveniently done by stirring it up with water and again throwing it on a filter.

Erythrin, or erythric acid,  $C_{20}H_{22}O_{10}$ , is almost insoluble in cold water, and requires two hundred and forty parts of boiling water for solution; on cooling, it is deposited in the form of a colourless crystalline powder, which is only slightly soluble in cold ether and alcohol, but more soluble

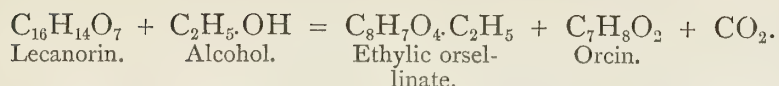


in hot alcohol, from which it crystallises in stellate groups of needles. The alcoholic solution is colourless, tasteless, and inodorous. Erythrin is soluble in solutions of caustic and carbonated alkalis, and in lime and baryta water. On the addition of an acid to any of these solutions it is thrown down unchanged as a bulky, white, gelatinous precipitate; but if the solutions are boiled, or if they are kept for any length of time, the erythrin is decomposed and is no longer separated on the addition of an acid. Its ammoniacal solution becomes red on exposure to the atmosphere. The alcoholic solution gives a white precipitate with subacetate of lead, but none with the neutral acetate: on the addition of perchloride of iron it acquires a beautiful purple or violet colour.

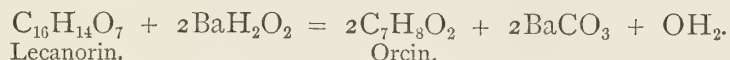
The researches of Schunck, published in 1842, threw much light on the composition of this compound, showing the relation that existed between the orcin of Robiquet, and Heeran's erythrin and 'pseudo-erythrin' (ethylic orsellinate). At the same time he proved that orcin was the only immediate colour-producing principle of the series. On boiling erythrin with weak baryta water, he found that it was decomposed into two substances, one of which he named *picroerythrin*, and the other he recognised as the orcin of Robiquet. The following equation will show the decomposition:—



*Lecanoric Acid*.—Schunck, by exhausting *Variolaria orcina* and other lichens of the genera *Lecanora* and *Variolaria* with ether, obtained a white crystalline substance to which he gave the name of lecanorin or lecanoric acid,  $\text{C}_{16}\text{H}_{14}\text{O}_7$ . When this substance is boiled with alcohol for some hours orcin is separated, and an ether formed which is identical with the pseudo-erythrin of Heeran. The decomposition is as follows:—



Schunck also found that when lecanorin is boiled with baryta water it is decomposed with formation of orcin and barium carbonate.



Lecanorin or lecanoric or orsellic acid may be obtained from the *Lecanora tartarea* or *Roccella tinctoria* by macerating it with milk of lime in a manner similar to that employed for the preparation of erythrin, but according to Hesse\* it is then contaminated with a yellowish brown colouring matter, from which it is extremely difficult to separate it. He prefers, therefore, to exhaust the lichen with ether, and after removing the latter by distillation the pale green crystalline residue is dissolved in milk of lime, and after being allowed to settle, the clear liquor is syphoned off and carefully neutralised with sulphuric acid. The precipitate thus obtained is recrystallised from hot alcohol, which on cooling deposits the lecanoric acid in the form of prismatic crystals. To obtain it quite pure, the crystals are treated with a quantity of ether, insufficient to dissolve the whole, and filtered. The residue left on evaporation is then dissolved in hot alcohol, from which the pure acid separates on cooling.

Crystallised lecanoric acid has the composition  $\text{C}_{16}\text{H}_{14}\text{O}_7 + \text{OH}_2$ , but the water is easily removed by heating it to  $212^\circ \text{F}$ . It is insoluble in cold water, but freely soluble in hot alcohol and in ether. Its solution reddens litmus. It dissolves readily in alkaline solutions, from which it is reprecipitated on the addition of an acid; if, however, it has been boiled or allowed to stand some considerable time before adding the acid, no precipitate is obtained, the lecanoric acid having become changed into orsellinic acid.

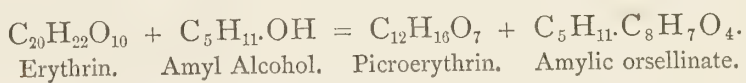
---

\* Ann. Chem. Pharm., cxxxix., 22.

It is insoluble in all weak acids except acetic. It yields a fugitive red colour with bleaching powder, and its alcoholic solution gives a crimson colour with persalts of iron. Strong nitric acid converts it into oxalic acid. It yields salts with metallic oxides. When heated in the open air on platinum foil, it melts and then catches fire, but in a closed tube it gives off a dense vapour, which condenses in the upper part of the tube, and after a time solidifies to a crystalline mass of orcin.

As already stated, when lecanoric acid is boiled with alcohol it yields *ethylic orsellinate*. This ether may also be conveniently prepared from erythrin by boiling it for some hours with eight parts of absolute alcohol, evaporating, and crystallising the residue (which consists of the ether, mixed with picroerythrin and resinous matters) from water. The ether may be obtained quite pure by recrystallisation from benzene. It is but slightly soluble in cold water, and crystallises from its solution in hot benzene, or boiling water, in colourless plates or needles. It is very soluble in alcohol or ether, and also in dilute alkalis, being precipitated unchanged from the latter on the addition of an acid. Its ammoniacal solution on exposure to the atmosphere assumes a wine-red tint. Stenhouse has prepared the corresponding methyl compound by a similar process, and has also examined the iodine substitution products of the two ethers.

When erythrin is boiled with amylic alcohol, *amylic orsellinate* and picroerythrin are formed.



On distilling off the excess of the alcohol, and boiling the residue with water, the picroerythrin dissolves and crystallises out on cooling in white silky needles, of the formula  $\text{C}_{12}\text{H}_{16}\text{O}_7, 3\text{OH}_2$ . This is the best method of preparing this substance in the pure state.



Picroerythrin, as already mentioned, was discovered by Schunck, who obtained it from the products of the decomposition which erythrin undergoes when boiled with water. It is only slightly soluble in cold water, but readily in hot, being deposited, on cooling, either in the form of needles or of shining plates. With perchloride of iron it produces a beautiful purple colour. It yields a precipitate with subacetate of lead, but none with the neutral acetate. When dissolved in ammonia and exposed to the atmosphere it gives, like lecanorin, a red colouring matter. Cold alkaline solutions readily dissolve picroerythrin, but when boiled it is decomposed with formation of orcin, erythrite, and an alkaline carbonate, as shown in the following equation :



Heated alone in a tube it yields a sublimate of orcin.

For a long time it was a matter of doubt, and gave rise to much discussion as to whether the lecanoric acid described by Schunck, and the  $\alpha$  and  $\beta$  orsellic acids obtained by Stenhouse, respectively from South American, and South African *Rocella*, were different compounds or not. The latter chemist, however, after a long series of experiments, has satisfactorily established that all three acids are identical.\*

*Erythrite*, *erythromannite*, or *pseudo-orcin*, derives its name from ἔρυθρος red, in allusion to the red colour obtainable from the lichen. This beautiful substance, which was discovered by Stenhouse, is interesting not only as being obtained from one of the most important of the colour-giving principles of the lichens, but also from its chemical relations, and from the various products obtained by the action of reagents on it. It is not only formed by the decomposition of erythrin, or rather from the picroerythrin obtained by the splitting up of the erythrin, but it also

\* Jour. Chem. Soc., xx., 221.

exists ready formed in the *Protococcus vulgaris*, from which it may be readily extracted. The method of preparing erythrite from erythrin has already been described when treating of orcin.

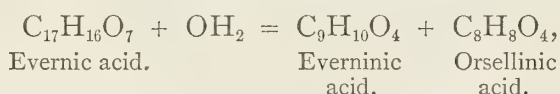
When pure it crystallises in large colourless prisms belonging to the dimetric system, which are readily soluble in water, but only slightly so in alcohol; it is insoluble in ether. As it possesses a slightly sweet taste, Berthelot was led to consider it as a sugar. This view, however, is incorrect, its chemical reactions and decomposition showing that it is a true tetratomic alcohol. It does not reduce ammonia tartarate of copper, and it has no rotatory power on polarised light. It fuses at  $248^{\circ}$  F., and may be heated to  $482^{\circ}$  F. without undergoing decomposition. When mixed with twelve times its weight of concentrated hydriodic acid and distilled, it yields butylic iodide  $C_4H_9I$ . By the action of a mixture of concentrated nitric and sulphuric acids it is converted into a nitric ether, *tetranitroerythrite*,  $C_4H_6O_4(NO_2)_4$ , which is very explosive, detonating sharply when struck. By prolonged treatment with nitric acid, oxalic acid is produced, but no mucic acid. On fusing erythrite with potassium hydrate, hydrogen is evolved, and acetate and oxalate of the alkali produced.

*Usnic Acid, Evernic Acid, and Cladonic Acid.*—The first of these, *usnic acid*,  $C_{18}H_{18}O_7$ , which exists in the various species of *Usnea*, as well as in the *Ramalina* and *Evernia*, was discovered by Knop, and has since been carefully examined by Stenhouse, and by Hesse. It may be readily prepared from the *Usnea florida* by extracting it with milk of lime and precipitating the solution by hydrochloric acid. The impure usnic acid thus obtained may be purified by dissolving it in hot alcohol to which caustic soda has been added, filtering, and then adding excess of acid. After being collected and washed with cold alcohol, it should be recrystallised from boiling alcohol, in which it is only

sparingly soluble. It forms bright yellow needles which melt at 397° F.

By extracting *Evernia prunastri* with milk of lime in the usual way, a mixture of usnic acid and *evernic acid*  $C_{17}H_{16}O_7$  is obtained, from which the latter may readily be separated by treating the product with hot alcohol. This leaves the comparatively insoluble usnic acid, but dissolves the evernic acid, and deposits it again on cooling in minute colourless crystals, which, after being purified by recrystallisation melt at 327° F.

By the action of alkalis, evernic acid is decomposed with formation of *everninic acid*, and probably also orsellinic acid,

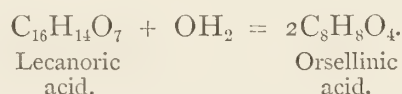


the latter being resolved by the continued action of the alkali into orcin and carbonic acid. Everninic acid is readily prepared from evernic acid by boiling it with baryta water, and then adding a slight excess of hydrochloric acid to precipitate the new compound. It closely resembles benzoic acid in appearance, and is only sparingly soluble in cold water, but readily in alcohol or ether. It melts at 296° F. When evernic acid is boiled with absolute alcohol, everninic ether,  $C_2H_5 \cdot C_9H_9O_4$  is formed, so that unless care be taken in crystallising the acid from hot alcohol considerable loss is apt to occur.

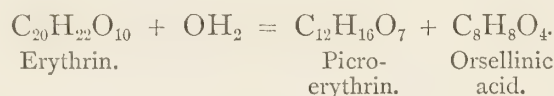
*Cladonic Acid*,  $C_{18}H_{18}O_7$ , the  $\beta$ -*usnic acid* of Hesse, is isomeric with ordinary usnic acid, which it closely resembles in appearance. It is obtained from the *Cladonia rangiferina* by extracting it with a dilute solution of caustic soda, precipitating by hydrochloric acid and recrystallising the product alternately from ether and from alcohol. It melts at 347° F., or about 50° lower than ordinary usnic acid, from which it differs in yielding a sublimate of  $\beta$ -*orcin*  $C_8H_{10}O_2$ , a homologue of orcin, when distilled.



*Orsellinic Acid, or Orsellesic Acid.*—This acid was discovered by Stenhouse in 1848, and although it does not exist ready formed in the lichens, yet it may readily be obtained from both erythrin and lecanoric acids, two of the colour-giving principles of the lichens, and possibly also from evernic acid. These compounds, when heated for a short time with a solution of an alkali or an alkaline earth, or even by the long-continued action of boiling water itself, yield orsellinic acid. The decomposition which evernic acid undergoes under these circumstances has just been noticed; that of lecanoric acid is exhibited in the subjoined equation.

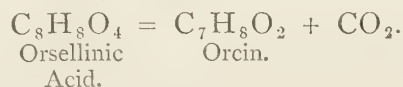


When erythrin is boiled with water containing lime or baryta it splits up, yielding picroerythrin and orsellinic acid.



The most convenient way of preparing orsellinic acid is to dissolve lecanoric acid in baryta water, avoiding excess of the latter, and then to boil the solution for a short time; care must be taken, however, that the action does not proceed so far as to decompose the orsellinic acid into orcin and carbonic acid. On adding hydrochloric acid to the solution, the new compound is thrown down as a gelatinous precipitate, which may be purified by crystallisation from water or from alcohol.

Pure orsellinic acid,  $\text{C}_8\text{H}_8\text{O}_4$ , forms colourless prismatic crystals, which melt at  $349^\circ \text{F.}$ , and are much more soluble in water and alcohol than lecanoric acid. It is readily decomposed by boiling with alkalis, orcin being formed.



The orsellinates of the alkalis, and of barium and calcium are readily soluble in water.

Besides the compounds already described as obtained from the colour-producing lichens, Schunck found that *parellic acid*,  $C_9H_6O_4$ , sometimes accompanied lecanoric acid. *Roccellinin*,  $C_{18}H_{16}O_7$ , and *roccellic acid*,  $C_{17}H_{32}O_4$ , a kind of fatty acid, have also been obtained from the *Roccella tinctoria*, whilst  $\beta$ -erythrin,  $C_{21}H_{24}O_{10}$ , was discovered by Menshutkin\* in a South American variety of the *Roccella fuciformis*. It differs from ordinary erythrin by yielding as the ultimate products of its decomposition erythrite and  $\beta$ -orcin.

The following summary of the principal facts in connection with the colour-giving principles of the lichens may be found useful :

1. Lecanoric acid, by the action of alkalis, takes up water, and is converted into orsellinic acid, which subsequently splits up into carbonic anhydride,  $CO_2$ , and orcin.

2. Erythrin, by the action of alkalis, yields orsellinic acid and picroerythrin, the latter of which is then decomposed into erythrite, orcin, and carbonic anhydride.

3. Everinic acid, by the action of alkalis, yields everinic acid and orcin; the latter, as has been already noticed, being possibly derived from orsellinic acid as an intermediate product of the reaction.

CUDBEAR.—The best weed for the preparation of *cudbear* is the *Lecanora tartarea*. It is ground up with ammonia, at 4° Twaddle, into a paste, and allowed to ferment in a similar manner to orchil. When the fermentation is complete, the mass is dried in troughs, through which hot water pipes are passed, and in which a roller fitted with small arms revolves, so as to allow the ammonia and water to evaporate more easily. When dry it is powdered, and is ready for the market. It is principally

---

\* Bull. Soc. Chim., [2], ii., 424.

used, either alone or with other dyestuffs, for dyeing woollen goods maroon and various shades of brown.

Cudbear is occasionally adulterated with common salt, and magenta is sometimes added to improve the colour.

LITMUS.—The colour called litmus, or lacmus, employed by chemists to detect the presence of free acid or alkali, is, according to Kane, a mixture of several colouring matters, *azolitmin*,  $C_7H_7NO_4$  *erythrolëin*, *erythrolitmin*, and *spaniolitmin*. De Luynes has succeeded in preparing azolitmin directly from orcin, by boiling one part of that substance with twenty-five parts of crystallised carbonate of soda, five of water, and one of a strong solution of ammonia. The whole is maintained at a temperature of  $140^\circ$  to  $167^\circ$  in a closed vessel, and frequently agitated. A blue liquor is thus produced, which is diluted with water, and hydrochloric acid added in slight excess. The precipitated colouring matter after being washed and dried, is considered by De Luynes to be pure azolitmin. It is a blue substance which acquires a coppery lustre when rubbed with the nail. The following equation is intended to illustrate the conversion of orcin into azolitmin :—



Azolitmin is almost insoluble in cold water, benzene, or oil of turpentine, but dissolves readily in alcohol, to which it imparts a red colour. When neutralised with an alkali it becomes blue, but is again turned red on the addition of an acid in very slight excess.

Litmus is manufactured in Holland from the same varieties of lichen as those employed in the production of orchil. The weed is ground and mixed with ammonia and carbonate of potash, and left to ferment until the mass has acquired a purple tint. Lime, potash, and urine are then added, and the whole left until the colour is changed to blue. Plaster of Paris is now mixed with it, and it is



moulded into small cubes which, when dried, are ready for use.

A peculiar blue colour which has a great similarity to litmus, called *tourne-sol en drapeaux*, is manufactured principally at Grand-Gallargues, in the south of France, from a species of Euphorbiaceæ, called *Croton tinctorium*. The sap of the plant is pressed out, and coarse linen is dipped into it, and then placed over vats containing putrid urine to which lime and alum have been added. The cloths, which are moved from time to time, gradually assume a dark blue colour. They are then dipped a second time in the sap, to which some urine has been added, and are dried in the sun.

These blue cloths are sent to Holland, where they are used for giving a red colour to the outside rind of cheese.

RESORCIN.—This compound has a very close relation to orcin, the latter in fact being a methyl derivative of the former; for resorcin,  $C_6H_4(OH)_2$ , is a di-hydroxyl derivative of benzene; whilst orcin,  $C_6H_3(CH_3)(OH)_2$ , is the corresponding derivative of toluene, which is methyl benzene. As might be expected, it yields colouring matters similar to those obtained from orcin, by exposure to the air in presence of ammonia, but these, which are of a much redder shade than orchil, have not come into general use.

Resorcin may be prepared in a variety of ways, as by fusing with potassium hydrate certain resins such as galbanum, asafoetida, gum ammoniacum, and sagapenum, the first mentioned giving the most satisfactory results. In order to extract the resorcin from the fused product it is dissolved in water as soon as it is cold, neutralised with sulphuric acid, and the clear filtered solution shaken up with ether. This takes up the resorcin, which is deposited in the crystalline state on distilling off the ether. It may be purified by distillation. Besides these resins, other substances, when fused with caustic alkalis, yield resorcin, such

as paraphenolsulphonic acid, bromobenzenesulphonic acid, paraiodophenol, and brazilin. Kopp, however, considers the best and cheapest method of preparing this substance to be by the dry distillation of the impure brazilin lake, formed by adding chalk to the wash waters obtained in the manufacture of brazilin from Brazil wood extract, and evaporating to dryness.

Resorcin is a colourless crystalline compound, closely resembling orcin in its properties and appearance, being very soluble in water, alcohol, and ether. It melts at  $210^{\circ}$  F., and distils without decomposition at  $513^{\circ}$  F.

The behaviour of resorcin with fuming sulphuric acid is very characteristic. It dissolves at first with an orange-yellow colour, which in the course of twenty or thirty minutes changes to a greenish-blue, and ultimately to a pure blue. On warming this solution to  $212^{\circ}$  F. it changes to a fine purple-red.

*Azoresorcin derivatives.*—Weselsky,\* by treating resorcin with nitrous acid, has succeeded in obtaining colouring matters which rival the aniline colours in the brilliancy and purity of their shades. *Diazaresorcin*,  $C_{18}H_{12}N_2O_6$ , is obtained in brown granular crystals, with a green metallic lustre, on passing nitrous acid into an ethereal solution of resorcin. It is only sparingly soluble in water, but dissolves in alcohol or acetic acid, forming a dark cherry-red coloured liquid; its alkaline solutions are of a splendid blue-violet. The action of strong sulphuric or hydrochloric acid on this substance gives rise to *diazaresorufin*,  $C_{36}H_{18}N_4O_9$ , which forms small dark red crystals, almost insoluble in water, alcohol, or ether, but dissolving in alkaline solutions with a magnificent crimson colour. When heated with tin and hydrochloric acid, diazaresorufin undergoes reduction, the solution becomes emerald-green, and on cooling deposits pale green needles of *hydrodiazo-*

---

\* Deut. Chem. Ges. Ber., iv., 613.

*resorufin hydrochloride*,  $C_{36}H_{30}N_4O_9$ ,  $3HCl$ , which assume the coppery lustre of indigo when exposed to the air.

On heating diazoresorcin with strong nitric acid it is converted into *tetrazoresorcin nitrate*,  $C_{18}H_6N_4O_6$ ,  $(NO_3)_3$ , which crystallises in garnet-red needles with a brilliant metallic lustre. They are soluble in water and alcohol, and very readily in ether, with a pure indigo-blue colour. By the further action of nitric acid they are converted into *tetrazoresorufin nitrate*,  $C_{34}H_6N_8O_9$ ,  $(NO_3)_6$ , the crystals of which closely resemble permanganate of potassium in appearance, and dissolve in water, alcohol, and ether, yielding solutions of a similar colour. These compounds when treated with reducing agents yield new products.

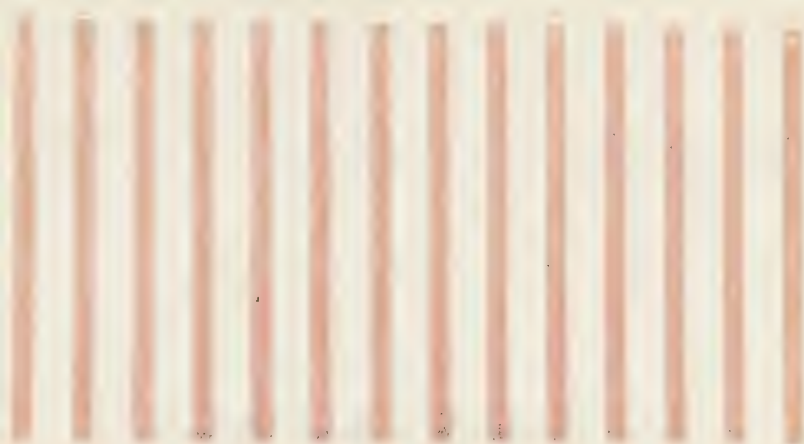
*Fluoresceïn*.—This a compound discovered by Baeyer,\* and subsequently examined by Fischer.† It is prepared by heating 2 molecules of resorcin with 1 of phthalic anhydride to a temperature of about  $390^\circ$  F. for several hours. A reaction soon sets in, accompanied by the revolution of aqueous vapour, and the mass ultimately becomes solid as soon as it is cold. The dark red product is powdered, and boiled with water to remove unaltered resorcin and phthalic anhydride, and if required in a pure state may then be crystallised from alcohol, although with difficulty.

Pure fluoresceïn,  $C_{20}H_{12}O_4$ , is a red crystalline powder, which is almost insoluble in water or ether, and but slightly soluble in alcohol. It is soluble in alkaline solutions, that with ammonia being characterised by a beautiful green fluorescence. Fluoresceïn produces a fine yellow on wool and silk without a mordant. The accompanying beautiful specimen, which we owe to the kindness of M. H. Koechlin, is obtained by tetrabromo-fluoresceïn, or eosin, fixed with a salt of lead.

---

\* Deut. Chem. Ges. Ber., iv., 662, and † vii., 1211.





COLOUR OBTAINED WITH EOSIN.

When fluoresceïn is heated with concentrated sulphuric acid, at  $212^{\circ}$  for some time, and the product poured into water, a substance is precipitated which may be obtained in bright red prismatic crystals, and dissolves in alkalis with a blue colour; this is changed to red by the reducing action of zinc dust, and fabrics dipped into this liquid and exposed to the air become dyed blue, as in the indigo vat. The colour, however, is dull and not fast.

## CHAPTER IX.

QUERCITRON, FUSTIC, PERSIAN-BERRIES, WELD, ALOES, TURMERIC, ANNATTO, ILIXANTHIN, ETC., AND LA-KAO.

This chapter will be devoted principally to a consideration of some of the most useful and important yellow colouring matters used by dyers and calico printers. Besides this, it has been thought advisable to give a short notice of certain yellow-coloured compounds of vegetable origin, which, although they are not commercially of great importance, yet are interesting from a scientific point of view.

QUERCITRON.—Among the most valuable of the yellow dyes is *quercitron*, the inner bark of a peculiar species of oak, called the *Quercus nigra*, or *tinctoria*. This tree is indigenous to the United States, and is especially found in the forests of Pennsylvania, Georgia, and in North and South Carolina. A chemist of the name of Bancroft first introduced it to the English dyers in the year 1775, and obtained by Act of Parliament the exclusive right of importing this wood. The most esteemed qualities are those shipped from Philadelphia, New York, and Baltimore.

The bark, after being removed from the tree, is dried, and ground between mill-stones; its value being in proportion to the depth of colour and fineness of the powder, for the woody fibre of the bark contains but a comparatively small quantity of the colouring principle, and is not easily reduced to a fine powder.

A freshly prepared decoction of the bark is transparent, and of a dull orange-red colour, but after a time it becomes

turbid, and yields a yellow crystalline deposit. The supernatant liquor gradually becomes gelatinous, acquiring at the same time a blood-red colour, from this it may be inferred that a slow, but gradual change has taken place, no doubt due to the glucoside being decomposed by a peculiar ferment. As the colouring matter thus liberated is rapidly oxidised, and becomes useless as a colour-giving principle, it is important that the decoction should be used as soon as possible after its preparation.

A freshly made solution gives the following reactions:—

|                       |   |
|-----------------------|---|
| Alkalis.              | Deepen the colour.  |
| Lime Water.           | { Deepens the colour and gives a brownish-yellow flocculent precipitate.                  |
| Alum.                 | { Brightens the solution, forming a slight precipitate.                                   |
| Protochloride of tin. | Brown precipitate.  |
| Bichloride of tin.    | Yellowish precipitate.  |
| Acetate of lead.      | { Thick brownish-yellow flocculent precipitate.   |
| Acetate of copper.    | { Olive green precipitate, the liquor becoming yellowish-green.                           |
| Salts of iron.        | { Colour the solution green, and afterwards give an olive-brown flocculent precipitate.   |
| Acids.                | { Brighten the liquor and give rise to a brown flocculent precipitate.                    |
| Acetic acid.          | { Decreases the intensity of the colour, but if the liquor is turbid it renders it clear. |
| Gelatin.              | Reddish flocculent precipitate.   |
| Chlorine.             | { Abundant flocculent precipitate. An excess of the reagent decolorises the liquor.       |

Chevreul was the first chemist who examined this dye-



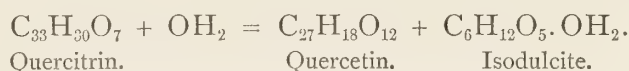
stuff, and he found it to contain, besides a peculiar tannin, which has since received the name of *quercitannic acid*, a yellow colouring principle to which he gave the name of *quercitrin*. This he obtained from quercitron bark by boiling it with water and allowing the solution to stand, when fine laminated crystals were deposited. Bolley\* prepares it by exhausting the bark with alcohol, and after precipitating the tannin by gelatin, he concentrates the solution by evaporation, and recrystallises the quercitrin which separates, from boiling alcohol. It is, however, far more advantageously prepared from the flavin imported from America, some samples of which consist of almost pure quercitrin. On boiling this dyestuff with water and filtering, a solution is obtained, which, on cooling, deposits quercitrin in the crystalline state. Quercitrin forms minute rhombic plates of a pale yellow colour, which are only slightly soluble in ether or cold water, but more readily in boiling water, and easily in alcohol. Alkaline solutions dissolve quercitrin with a greenish-yellow colour which becomes brown on exposure to the atmosphere. The aqueous solution gives a brownish-yellow precipitate with baryta, whilst lime water imparts to it a fine yellow tint. The acetates of copper and lead give a bright yellow precipitate. Its most characteristic reactions, however, are with perchloride of iron, which gives a greenish-yellow precipitate, and with protochloride and oxymuriate of tin, with which it gives beautiful bright yellow precipitates.

Rigaud discovered some years ago, that when quercitrin was boiled with water containing 10 per cent. of sulphuric acid, it was decomposed into a body to which he gave the name of *quercetin*, and a species of sugar to which he assigned the formula  $C_6H_{12}O_6$ , thus proving it to be a glucoside. The quercetin separates in flocks which, after

---

\* Ann. Chem. Pharm., xxxvii., 101.

being collected and washed, are crystallised from alcohol. The decomposition which takes place when quercitrin is boiled with acids may be thus represented :



To isolate the saccharine matter, the acid liquid from which the quercetin has been separated is neutralised with baryta to remove the sulphuric acid, and then evaporated, when the sugar is obtained in the crystalline state. Hlasiwetz and Pfaundler, who subsequently examined this subject, found that the sugar, which they call *isodulcite*,  $\text{C}_6\text{H}_{12}\text{O}_5 + \text{OH}_2$  is incapable of fermentation, although it reduces cupric salts. It is isomeric with mannite and dulcite, and when treated with a mixture of concentrated nitric and sulphuric acids it yields a trinitro derivative.

Quercetin, or its glucoside quercitrin, has been found in a great variety of plants. Rochleder\* showed that it exists in the flowers and ripe fruit of the horse chestnut (*Aesculus hippocastanum*). The robinin obtained by Zwenger and Dronke† from the *Robina pseudacacia*, although differing from quercitrin, when boiled with acid, splits up into quercetin and sugar. Robinin is also found in the flowers of the *Carvus mascula*.

Quercetin,  $\text{C}_{27}\text{H}_{18}\text{O}_{12}$ , crystallises in slender needles of a bright yellow colour, and of a much richer hue than quercitrin. It has no taste, is insoluble in cold, and only slightly soluble in hot water, but is freely soluble in alcohol and in acetic acid. It is also soluble in alkalis, to which it communicates an orange-yellow hue. Its alcoholic solution gives orange precipitates with the salts of lime, baryta, and lead. It assumes an orange colour with perchloride of tin, and gives a green coloration with perchloride of iron.

---

\* Chem. Centr., iv., 162.

† Ann. Chem. Pharm. Supplement, i., 257.

Quercetin is decolorised by nascent hydrogen. It dissolves in concentrated sulphuric acid, forming an acid which dyes woollen a fast yellow colour without a mordant. Schützenberger and Bertéche have obtained a crystallisable acetic derivative of quercetin by heating it with acetic anhydride. It contains three or four acetyl groups,  $C_2H_3O$ , in place of the same number of hydrogen atoms.

According to Hlasiwetz and Pfaundler\* a potassium compound of quercetin, having the formula  $C_{27}H_{18}O_{12}K_2O$ , is obtained on dissolving one part of quercetin in a concentrated solution of three parts of potassium carbonate, and allowing the solution to cool. It crystallises in slender yellow needles, which cannot be dissolved without decomposition. The corresponding sodium compound has the composition  $C_{27}H_{18}O_{12}Na_2O$ .

The same chemists have studied the action of potassium hydrate on quercetin, and find that when one part of this substance is added to a boiling solution of three parts of caustic potash in one of water, and the whole evaporated to dryness, a product is obtained which consists of *paradatis-cetin*, *phloroglucin*, and *quercetic acid*. In order to isolate these, the mass, as soon as it is cold, is dissolved in water and neutralised with hydrochloric acid, which precipitates the paradatis-cetin together with some unaltered quercetin. The filtered liquid is then mixed with one-quarter its bulk of alcohol, and agitated with ether which dissolves the phloroglucin and quercetic acid. To separate these two, the residue left on the evaporation of the ethereal solution is dissolved in water, and basic acetate of lead added; this precipitates the quercetic acid, and the clear solution, after the removal of the excess of lead by sulphuretted hydrogen, and evaporation, yields phloroglucin in the crystalline state. The lead quercetate, after being washed, is suspended in water, decomposed by sulphuretted hydrogen,

---

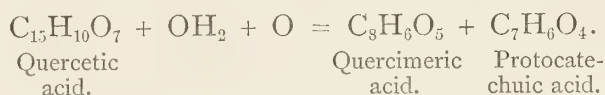
\* Jour. für Prak. Chem., xciv., 65.



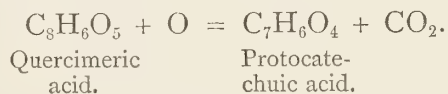
and the lead sulphide separated by filtration: the aqueous solution, when evaporated *in vacuo*, yields crystallised quercetic acid. The paradatiscetin may be purified by dissolving it in alcohol and precipitating the unaltered quercetin by lead acetate: the alcoholic solution, after the excess of lead has been separated by sulphuretted hydrogen, is concentrated by evaporation, and the paradatiscetin precipitated by the addition of water.

*Quercetic acid*,  $C_{15}H_{10}O_7$ , crystallises in fine white, silky needles, which are only slightly soluble in cold water, but freely soluble in alcohol, ether, or hot water. Its solution, which has an astringent taste, gives a dark blue coloration with perchloride of iron. An alkaline solution when exposed to the air assumes a magnificent crimson colour. Quercetic acid dissolves in sulphuric acid with a reddish-brown tint.

By the prolonged action of potassium hydrate on quercetin, or better, when quercetic acid is fused with potash, a new acid called *quercimeric acid*,  $C_8H_6O_5$ , is produced.



It forms small prismatic crystals, which are readily soluble in water, alcohol, and ether. When fused with potash it yields protocatechuic acid thus:—



*Paradatiscetin*,  $C_{15}H_{10}O_6$ , which is isomeric with datiscetin, a substance extracted by Stenhouse from the *Datisca cannabina*, is deposited from an alcoholic solution in yellowish needles, which are only slightly soluble in water, but very soluble in alcohol or ether. Its alcoholic solution gives an intense purple colour with perchloride of iron. The alkaline solution has a bright yellow colour, which changes

to green when exposed to the atmosphere. Bromine imparts to a solution of paradatiscetin a red colour, which changes after a little while to a magnificent crimson, whilst chlorine and bleaching powder give a reddish-brown coloration. Paradatiscetin forms definite compounds with bases; those of barium and strontium crystallising well.

*Phloroglucin*, which was originally obtained as a product of the decomposition of phloretin, separates from its aqueous solution in hydrated crystals, belonging to the trimetric system, and having the formula  $C_6H_6O_3 \cdot 2OH_2$ . They effloresce in dry air, and lose their water of crystallisation at  $192^\circ F.$ , or *in vacuo* over sulphuric acid.

Phloroglucin has a sweeter taste than sugar, and undergoes no change in contact with the air. It melts at  $428^\circ F.$ , and may be sublimed at a higher temperature without decomposition. It dissolves in water and alcohol, and still more readily in ether. It gives a precipitate with subacetate of lead, but none with other metallic salts. It easily reduces the nitrates of silver and mercury, especially on the addition of ammonia and the application of heat. With perchloride of iron it gives a deep red coloration, and with bleaching powder a yellow tint, which, however, soon disappears. Ammoniacal phloroglucin shaken up with air becomes reddish-brown, and afterwards opaque, giving rise to *phloramine*. Nitric acid converts phloroglucin into *nitrophloroglucin*.

When a solution of quercetin in soda is treated with sodium amalgam, it acquires a dark brown colour, which gradually turns to yellow. If hydrochloric acid be then added and the whole shaken up with ether, this extracts three compounds, namely, phloroglucin, a soluble substance having the formula  $C_7H_8O_3$ , and a third which crystallises from hot water in slender prisms, having the composition  $C_{13}H_{12}O_3$ . Both these bodies yield protocatechuic acid when fused with potash.

When an alcoholic solution of quercetin acidulated with hydrochloric acid is acted on by sodium amalgam, the liquid assumes a fine purple colour, and on concentration yields fine red prismatic crystals analogous to isomarin, a product obtained from moric acid, one of the colouring matters of old fustic. It is easily oxidised and reconverted into quercetin by dissolving it in alcohol with the addition of a small quantity of alkali, and exposing it to the atmosphere. It becomes green by the action of alkalis, but re-assumes its red colour on the addition of acids.

FLAVIN.—Within the last twenty years a preparation of quercitron bark has been imported into this country from America under the name of *flavin*; it varies greatly, however, in composition, being sometimes nearly pure quercitrin, whilst other samples only contain quercetin. Bolley examined a specimen of this substance some years ago and found it to contain about 45 per cent. of quercetin, the remaining 55 per cent. consisting of woody fibre, together with a small quantity of a peculiar sugar, which was doubtless isodulcite. Flavin, therefore, is in some cases the product of the decomposition of quercitrin, the natural glucoside of the bark, by the action of an acid, and stands in the same relation to it that garancin does to madder. It is easy to understand why it is much cheaper for the dyer and calico printer to use this product than the bark itself, and also why it gives brighter colours. The quantity of colouring matter in flavin as compared with bark, is as sixteen to one, or, 1 oz. of flavin is equal to 1 lb. of bark.

It is now manufactured in England, but the quality is not so good as that imported from America, probably owing to the latter being prepared from the fresh wood. The details of the American process are kept secret, but that followed in England consists in adding 2 tons of bark to a mixture of 4 tons of water, with 2 cwt. of oil of vitriol, and passing steam through the mixture for twelve



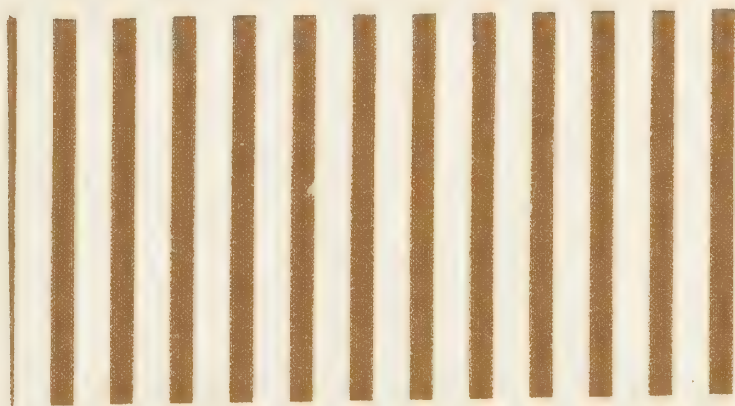
hours. When cold it is run upon woollen filters, and after being washed with water until all the sulphuric acid is removed, it is pressed, dried, and sieved.

Quercitron bark and flavin are chiefly used for dyeing woollen and mixed fabrics. To dye pieces of woollen goods of 22 or 23 lbs., the process and proportions are as follows: For each piece, 2 lbs. of alum and 1 lb. of tartar are put into a vat containing a sufficient quantity of boiling water, and flavin added according to the depth of shade required. The mixture is boiled for a few minutes, a pint of nitrate of tin per piece is then added, and the pieces are placed in the vat and boiled for about an hour. In mixed fabrics the pieces are first treated as above, then well washed until all trace of acid is removed, after which they are passed at width through a bath of sumach, then through muriate of tin, and finally through quercitron bark liquor and alum. If cotton alone is to be dyed, it is done cold, and a little oxymuriate of tin is added to the dyeing liquor. For the annexed sample we are indebted to the kindness of Messrs. Z. Heys and Sons, Barrhead, near Glasgow.



QUERCITRON YELLOW,

Neither quercitron bark nor flavin are much used in calico printing as a yellow dye, but are employed to impart brown and orange hues to madder and garancin, and to modify the shades produced by sumach, cochineal, and logwood. The mordant employed is either alum, or red liquor (an impure acetate of alumina). When used for this purpose the bath should have a temperature of about 120° or 130° F.; clear whites are then easily obtained. It is useful also to add a little gelatin to the liquor before using it to precipitate the quercitannic acid, which interferes with the brilliancy of the colours. It is used sometimes also for mixed colours, as in the accompanying sample, printed with a mixture of acetate of chromium, with extract of madder and quercitron, and for which we are indebted to the kindness of M. H. Koechlin.



EXTRACT OF MADDER AND QUERCITRON.

The best method of estimating the value of a sample of quercitron bark or flavin, is to dye some mordanted cloth in the same way as in testing the value of a madder or garancin.

FUSTIC.—This dyestuff is the wood of a tree belonging to the natural order *Urticaceæ*, called *Morus*, or *Machura*

*tinctoria*. It is known technically as yellow wood, or old fustic, the best qualities being imported from Cuba and Tampico. Those from the Antilles and Pernambuco are of inferior quality. Some very large logs arrive in this country from India, but they contain very small quantities of colouring matter and are principally used in cabinet-making.

A decoction of old fustic has a bitter, astringent taste, and gives the following reactions:—

|   |  |
|---|--|
| Alkalis.                                | Change the colour to a reddish-brown.  |
| Lime water.                             | Changes the colour to reddish-brown.   |
| Sulphuric, nitric,<br>and oxalic acids. | } Slight precipitates.   |
| Acetic acid.                            | } Makes the colour of the liquor paler<br>and brighter.  |
| Alum.                                   | Bright yellow precipitate.   |
| Ferric sulphate.                        | } Olive brown coloration, and, on stand-<br>ing, a brownish-black precipitate.                                 |
| Sulphate of copper.                     | Dark green precipitate.  |
| Protochloride of tin.                   | Golden-yellow precipitate.   |
| Acetate of lead.                        | Orange-yellow precipitate.   |
| Acetate of copper.                      | Brownish-yellow precipitate.   |
| Gelatin.                                | Orange-yellow flocculent precipitate.  |
| Chlorine.                               | } Slight precipitate, with a reddish<br>coloration which disappears when<br>an excess of chlorine is employed. |

In this case, again, Chevreul was the first to isolate the two colouring matters in the wood, the one soluble in water which he named *morin jaune*, the other nearly insoluble which he called *morin blanc*. He found that the latter compound gave with persalts of iron a dark red coloration, whilst the former assumed a greenish hue in the presence of these salts. In 1851, Wagner,\* considering these colour-

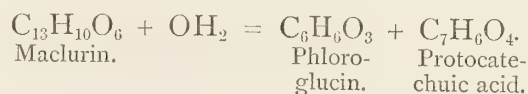
\* Jour. für Prak. Chem., li., 82.



ing matters to be acids, called the morin blanc, moric acid, and morin jaune, morintannic acid; the latter being identical with the crystalline compound observed by Chevreul in the interior of the logs.

Hlasiwetz and Pfaundler\* since then have very carefully studied these two compounds. In order to obtain them in a pure state, rasped fustic is boiled twice with water, and the solution concentrated to the state of a syrup, when, after a few days, a crystalline deposit takes place, which is collected, washed rapidly with cold water, and pressed. The product, which consists of morintannic acid and the calcium compound of moric acid or morin, is treated with boiling water, which leaves the latter, whilst the morintannic acid is dissolved. The insoluble lime compound, after being decomposed by treatment with weak hydrochloric acid, is dissolved in alcohol, from which, on the addition of two-thirds of its bulk of water, it is deposited in the form of yellow needles. To obtain the morintannic acid, the aqueous solution above described is concentrated, and the colouring matter which separates is recrystallised once or twice from water acidulated with hydrochloric acid.

*Morintannic acid*, or *maclurin*,  $C_{13}H_{10}O_6$ , as thus prepared, is a crystalline powder of a pale yellow colour which is freely soluble in water, requiring only 2.4 parts of boiling and 6.4 of cold. It is soluble in alcohol, ether, and wood spirit. It fuses at a temperature of  $392^{\circ}$  F. and is decomposed at  $480^{\circ}$ . When heated with a concentrated solution of caustic alkali, it yields phloroglucin and protocatechuic acid.



When a moderately concentrated solution of maclurin is heated with zinc and sulphuric acid, it rapidly assumes a red colour, which gradually changes to orange, and the

---

\* Ann. Chem. Pharm., cxxvii., 351.

solution then contains phloroglucin and a new substance, *machromin*,  $C_{14}H_{10}O_5$ .

Machromin crystallises in minute tufts of slender needles, and derives its name from the great variety of colours it yields. It is very slightly soluble in water or alcohol, but somewhat more so in ether. Both the crystals and their solutions become rapidly blue on exposure to the air, or in contact with oxydising agents. On adding hydrochloric acid, an amorphous blue precipitate is produced. The alkaline solution likewise assumes a blue colour on exposure to the atmosphere. With perchloride of iron or bichloride of mercury, a solution of machromin assumes a beautiful violet shade, which gradually passes into blue. Nitrate of silver gives a similar coloration, the silver salt being at the same time reduced. Machromin dissolves in sulphuric acid, forming an orange-coloured solution which becomes of an intense green on the application of heat; the colour is not changed by diluting it with water, but assumes a purple hue on the addition of an alkali.

The blue substance formed by the oxidation of machromin can be easily obtained by adding to an aqueous solution of that body an excess of perchloride of iron. Dark blue flakes are thus produced, which are collected, washed with water, and dried; after being washed with ether, the new colouring matter is obtained as a brilliant dark blue mass. Its formula appears to be  $C_{14}H_8O_5$ . Its alcoholic solution is decolorised by the action of zinc, or of sodium amalgam.

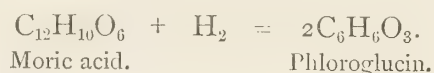
Maclurin when dissolved in alkalis and acted on by sodium amalgam, gives rise to phloroglucin and a new body having the formula  $C_{14}H_{12}O_5$ .

If maclurin is dissolved in sulphuric acid, after a short time brick-red crystals of *rufimoric acid* appear, which dissolve in ammonia with a purple coloration. The same acid is produced if maclurin is boiled with hydrochloric acid.

*Moric acid*, or *morin*, when pure, crystallises in colourless needles, which have the formula  $C_{12}H_{10}O_6$ . It is nearly insoluble in water and bisulphide of carbon, only slightly soluble in ether, but freely so in alcohol. It dissolves in solutions of the alkalis, borates, or phosphates with a yellow coloration, and is precipitated from them on the addition of an acid. Perchloride of iron communicates to its alcoholic solution an olive-green shade. It gives yellow precipitates with salts of zinc, tin, lead, and aluminium, and a dark green precipitate with those of copper.

Hlasiwetz has obtained well defined salts of this acid with potassium, sodium, calcium, barium, lead, and zinc. Moric acid absorbs ammonia, forming a yellow compound, whilst by the action of bromine it yields *tribromomoric acid*,  $C_{12}H_5Br_3O_6$ .

Moric acid is transformed into phloroglucin, either when submitted to the action of nascent hydrogen, or by fusing it with caustic alkalis. A solution of moric acid in dilute alkali, when treated with sodium amalgam, at first becomes blue, then green, and finally yellowish-brown; it now no longer gives a precipitate on the addition of an acid, and on examination will be found to contain phloroglucin. The following equation represents the reaction:—



When an alcoholic solution of moric acid, rendered acid by hydrochloric acid, is treated with sodium amalgam until it acquires an intense purple colour, and is then separated from the excess of sodium amalgam and evaporated, it yields brilliant purple crystals of *isomorin*, a body having the same composition as morin. Under the influence of alkalis this solution becomes green, and after a time moric acid is re-formed; this change takes place rapidly on boiling. A solution of isomorin mixed with alum offers a remarkable instance of dichroism. If it is diluted, it has a



yellow colour by transmitted light, whilst by reflected light it appears of an uranium green.

Hlasiwetz thus sums up the analogies between quercetin and moric acid.

1. Both substances yield a purple compound when the acidulated alcoholic solutions are acted upon by sodium amalgam.

2. Both substances yield phloroglucin when alkaline solutions are treated by sodium amalgam, although in the case of quercetic acid other bodies are simultaneously formed.

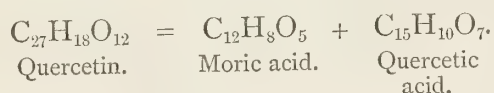
3. Both compounds combine with potash and soda.

4. Fused potash transforms both into phloroglucin.

5. Both bodies are decomposed by heat, yielding a similar sublimate.

6. Their solutions yield similar reactions with various reagents.

This eminent chemist believes that the similarity may be explained if we consider quercetin to be a compound of moric and quercetic acids, thus—

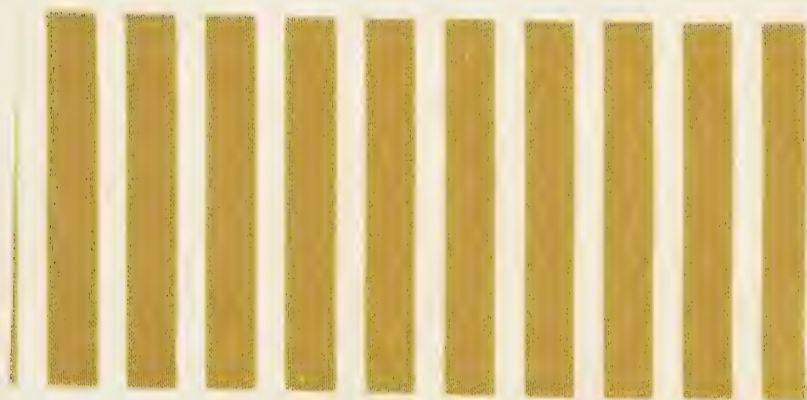


Goppelsröder\* has made a very interesting observation which may serve to distinguish moric acid from morintannic acid, namely, that a solution of moric acid becomes highly fluorescent on the addition of a small quantity of a salt of aluminium, whilst morintannic acid does not. This reaction is so delicate that moric acid becomes fluorescent by the addition of even one-eight thousandth part of alum, when a ray of light is passed through the solution by means of a lens, whilst if a solution contains only one-quarter millionth part of moric acid the fluorescence may still be seen. He suggests that advantage may be taken of this

\* Bull. Soc. Industrielle de Mulhouse, xxxvii., 899.

property as a means of testing for small quantities of salts of aluminium.

*Old Fustic* is especially used for dyeing wools in yellow and olive-green shades. They are mordanted with alumina for yellow, and with salts of iron for green. By the employment of salts of copper and other mordants, a variety of shades can be obtained. It is much used by dyers, but only to a limited extent by calico printers. If the morintannic acid or maclurin be precipitated by means of a little glue or gelatin, much brighter yellows are obtained with alumina mordants. The bright yellows produced by this dye are unfortunately affected by air and light, which communicate to them an orange hue. Through the kindness of Messrs. Z. Heys and Sons, of Barrhead, near Glasgow, we are enabled to illustrate the effect produced by Fustic.



FUSTIC.

YOUNG FUSTIC.—*Young fustic* is derived from a plant whose botanical name is *Rhus cotinus*, belonging to the same genus as sumach. It grows in the West Indies, the Levant, and also in France and the southern parts of Europe. It is found in commerce in the form of small logs and crooked branches, the wood imported from the West Indies and the Antilles being the finest in quality.

Young fustic contains a tannin matter, and three colour-giving principles, a red, a brown, and a yellow. The yellow colouring matter was first isolated by Chevreul, who gave it the name of *fustin*. Preisser states that he obtained it by first precipitating the tannin matter from a decoction of the wood by means of gelatin, filtering, and evaporating to dryness. The residue was treated with ether, and the ethereal solution, mixed with water and hydrate of lead, was placed in a retort, and the ether distilled off. A yellow compound was thus formed which was decomposed by sulphuretted hydrogen, and the liquor on evaporation yielded small yellow crystals of fustin, which were purified by crystallisation from ether. Bolley prepared it from a decoction of the wood by evaporating it to dryness and treating the residue with alcohol, this dissolved the fustin and left the red colouring matter and other substances. The alcoholic solution, on evaporation and addition of water, yields yellow crystals of fustin. He considers this colouring matter to be identical with quercetin, but Schützenberger doubts this, as fustin gives an orange-coloured precipitate with protochloride of tin, whilst quercetin gives a yellow one. Alkalis, moreover, produce a red coloration with fustin, and an orange-yellow with quercetin. Fustin is soluble in water, alcohol, and ether; its solutions oxidising rapidly when exposed to the atmosphere, and assuming an orange colour.

A decoction of the wood gives the following reactions:—

|                         |                                      |
|-------------------------|--------------------------------------|
| Alkalis.                | Communicate to it a fine orange hue. |
| Lime and baryta waters. | Bright orange precipitate.           |
| Acids.                  | Communicate to it a greenish hue.    |
| Protochloride of tin.   | Bright orange precipitate.           |
| Acetate of lead.        | Bright orange precipitate.           |
| Acetate of copper.      | Dark red precipitate.                |
| Ferric sulphate         | Olive-green precipitate.             |



Like fustin itself, the decoction of the wood becomes orange on exposure to the atmosphere.

Young fustic dyes wool mordanted with alumina a fine orange colour, but it is easily affected by light; its chief employment is in conjunction with cochineal, to the red colour of which it imparts a brilliant orange hue. It is not used in the dyeing of cotton goods, but is largely employed by tanners in Turkey and in the Tyrol to impart an orange-yellow colour to leather.

PERSIAN BERRIES.—These are the fruit of the buckthorn, and several varieties of *Rhamnus*, growing in the East, and in the southern countries of Europe, among which may be mentioned the *Rhamnus amygdalinus*, *R. oleoides*, *R. saxatilis*, growing in Persia and Turkey, and the *R. infectorius* growing in Avignon. Spain and the Morea also send considerable quantities to this country.

Generally speaking, the berries are gathered before they are quite ripe, to which their shrivelled appearance is due; they have a yellowish-green colour, and are about the size of small peas. They only give good results when quite fresh; after being kept a year or two they lose much of their value, yielding far less brilliant colours. The yellower they are, the lower the price they command in the market; whilst if they are brown or black, they are rejected as being old, or injured by damp. Amongst the dealers, they usually bear the name of the country from which they are imported; thus there are Avignoni berries, Turkish berries, &c.; amongst dyers and calico printers, however, all the varieties are called Persian berries, the best being imported from that country.

Persian berries have a disagreeable, bitter flavour, and an unpleasant odour. A freshly prepared decoction, which has a brownish-green colour, gives the following reactions:—

|          |                              |
|----------|------------------------------|
| Alkalis. | Change the colour to orange. |
| Acids.   | Render it slightly turbid.   |

|                          |   |
|--------------------------|---|
| Nitric acid.             | Brightens the liquor.   |
| Lime water.              | { Changes the colour to a greenish-yellow, causing a slight precipitate.  |
| Alum.                    | { Weakens the colour, but does not produce a precipitate.                 |
| Acetate of lead.         | { Causes no immediate change, but after a time the liquid becomes turbid. |
| Acetate of copper.       | Slight dirty yellow precipitate.  |
| Sulphate of copper.      | Colours the liquor greenish-yellow.                                       |
| Ferric sulphate of iron. | Colours the liquor greenish-yellow.                                       |
| Protochloride of tin.    | { Greenish-yellow coloration; slight precipitate.                         |
| Gelatin.                 | { Slightly turbid; a flocculent precipitate forming on standing.          |
| Chlorine.                | { Deepens the colour to red, afterwards changing it to yellow.            |

These berries yield to water three principles,—a very bitter compound, a red colouring matter which becomes brown on contact with the atmosphere, and a yellow colouring matter.

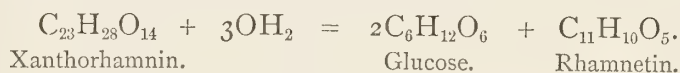
Kane was the first to carefully examine the colouring matters existing in Persian berries. For this purpose he extracted them with ether, and on evaporating the solution obtained fine golden-yellow crystals, to which he gave the name of *Chrysorhamnin*, and assigned to them the formula  $C_{23}H_{22}O_{11}$ . When a solution of this body was boiled in contact with the air, or in the presence of oxidising agents, he found that it was converted into a new substance very soluble in water, having the formula  $C_{23}H_{24}O_{14}$ . This substance, which he named *xanthorhamninn*, is also contained in the ripe berries, or in those that have been kept some time.

A few years afterwards Gellatly\* investigated this subject,

---

\* Edinburgh New Phil. Jour., vii., 252.

employing anhydrous ether, and obtained a substance which crystallised in pale yellow silky needles. It appears to be a different product to that obtained by Kane. Gellatly called it *Xanthorhamnin*, and considered it to have the formula  $C_{23}H_{28}O_{14}$ . He found also that when this body was boiled with dilute sulphuric acid it was decomposed into glucose, and a new colouring principle which, on cooling, is deposited from the liquid as a yellow crystalline powder. He gave it the name of *rhamnetin*, and represented the reaction which takes place by the following equation:—



He was certainly the first to point out the fact that the colouring matter of Persian berries was a glucoside. Hlasiwetz\* from a comparison of the analyses came to the conclusion that xanthorhamnin and rhamnetin were identical with quercitrin and quercetin.

Bolley† noticing the discrepancy between the properties of the xanthorhamnin described by Kane, and that described by Gellatly, re-examined these substances, and came to much the same conclusion as Hlasiwetz. Schützenberger and Bertéche subsequently studied the subject, but failed to throw any additional light on it. There can be no doubt that the product they obtained, and to which they gave the name of *chrysorhamnin*, is identical with the rhamnetin of Gellatly. They do not agree with Bolley in considering this compound to be identical with quercetin, nor do they believe xanthorhamnin to be the same body as quercitrin.

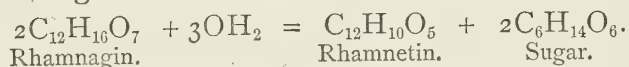
In 1866, Lefort, studying these questions, obtained two colouring matters from the berries, the first of which, a yellow crystalline body, he named *rhamnagin*, whilst the

\* Ann. Chem. Pharm., cxii., 107.

† Ann. Chem. Pharm., cxv., 55.



other, which he calls *ramnin*, is a yellow amorphous powder. In 1869 he published a paper stating that these two substances were isomeric, having the formula  $C_{12}H_{12}O_5 + 2OH_2$ . Rhamnagin is converted into rhamnin by the action of dilute acids without formation of sugar. According to Schützenberger, however, rhamnagin, when boiled with dilute sulphuric acid, is converted into rhamnetin, and a sugar isomeric with mannite.



We may conclude from the somewhat conflicting results of these various researches that there is in Persian berries a glucoside, crystallising in yellow silky needles, to which the following names and formulæ have been given:—

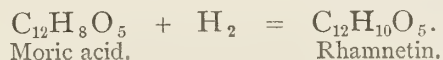
|                    |                             |           |
|--------------------|-----------------------------|-----------|
| Chrysorhamnin..... | $C_{23}H_{22}O_{11}$ .      | Kane.     |
| Xanthorhamnin ...  | $C_{23}H_{23}O_{14}$ .      | Gellatly. |
| Quercitrin .....   | $C_{33}H_{30}O_7$ .         | Bolley.   |
| Rhamnagin .....    | $C_{12}H_{12}O_5 + 2OH_2$ . | Lefort.   |
| Rhamninn .....     |                             |           |

This compound, on being boiled with sulphuric acid, yields a sugar and a yellow powder, to which the subjoined names and formulæ have been assigned:—

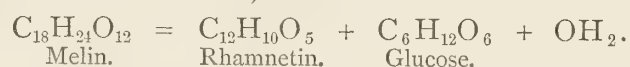
|                   |                        |                                 |
|-------------------|------------------------|---------------------------------|
| Rhamnetin .....   | $C_{11}H_{10}O_5$ .    | Gellatly.                       |
| Quercetin.....    | $C_{27}H_{18}O_{12}$ . | Bolley.                         |
| Chrysorhamnin ... | $C_{12}H_{10}O_5$ .    | Schützenberger<br>and Bertéche. |

Schützenberger and Bertéche have obtained a well defined acetyl derivative of rhamnetin by heating that body with anhydrous acetic acid, in closed tubes, to  $285^\circ F$ . They assign to it the formula  $C_{12}H_7(C_2H_3O)_3O_5$ . It has a pale yellow colour; is insoluble in water, but crystallises from alcohol.

Schützenberger remarks that the only difference between moric acid and rhamnetin, (or his chrysorhamnin) is that the latter contains two equivalents more of hydrogen.



M Kopp has also drawn attention to the fact that the *melin* or *rutin* obtained by Stein\* from the *Waifa* (the undeveloped flower buds of the *Sophora japonica*), may be considered as rhamnetin combined with one equivalent of glucose and one of water, thus :—



It will be readily perceived, even from this short notice, that the nature of the colouring matter of Persian berries is still involved in much obscurity. It is probable, however, that a careful comparison of the products of the decomposition of the glucosides found in this dyestuff, and in quercitron, would throw much light on the subject.

Persian berries are chiefly used by calico-printers for producing bright yellows or greens in steam styles. To obtain yellows, a freshly prepared decoction is mixed either with a little red mordant (sulpho-acetate of alumina) or with oxy-muriate of tin. The mixture is thickened, printed on, and the fabric steamed. The two samples, illustrating the effects obtainable with Persian berries, we owe to the courtesy of Messrs. Wood and Wright.



PERSIAN BERRIES (YELLOW).

---

\* Jour. für Prak. Chem., lxxxv., 351.



To produce greens, the decoction is mixed with prussiate of tin, thickened, printed on, and the fabric steamed. In this latter process, the prussiate of tin is decomposed, the tin uniting with the yellow colouring matter, whilst the hydroferrocyanic acid is decomposed, forming Prussian blue, the two colours together producing green on the fabric.



PERSIAN BERRIES (GREEN).

In woollen dyeing, the goods are first mordanted by being passed through a nearly boiling solution containing alum, and cream of tartar or salts of tin; the decoction of berries is then added, and the goods kept in until the required shade is obtained.

The decoction of berries is very apt to ferment and become ropy; but this may be prevented by the addition of a little carbolic acid.

A very brilliant yellow lake is also produced from Persian berries, the mode of manufacture was long kept secret by the Dutch. It was imported from Holland under the name of 'Dutch yellow.' It is obtained by preparing a decoction of the berries in water, in which a certain quantity of alum is dissolved; to this solution pure carbonate of



lime is added, which, as it falls, brings down with it the whole of the colouring matter. The shade of the lake may be varied by the addition of a little turmeric, fustic, quercitron, or dyewood to the alum solution. The lake thus produced is moulded into small lumps, which are dried in the shade. It is chiefly used by paper stainers, and for coarse decorations, such as theatrical scene painting, &c.

WELD.—Weld, *Reseda luteola*, is a variety of mignonette, which used to be cultivated in England, and is still grown in France, and other parts of the continent. It is an herbaceous plant, growing to a height of from 3 to 4 feet, which is sown in the spring of one year, and reaped in the autumn of the following year; being either pulled like flax or mown. It is dried in the shade, and has a yellow or greenish yellow tint according to the care bestowed on the drying. The upper parts of the plant contain the most colouring matter, especially the leaves and the external parts of the seeds. It is a very valuable dye when fixed on wool, both on account of the brilliancy of the colour produced, and also from its power of resisting light, heat, and acids.

A decoction of weld has a pale yellow colour when freshly prepared, but soon becomes turbid, and deposits a compound of the colour-giving principle with oxide of iron as a greenish-brown precipitate. When kept for some time, it assumes a reddish tint. It is slightly acid, and gives the following reactions:—

|                                       |   |
|---------------------------------------|---|
| Alkalis.                              | { Change the colour to a golden-yellow.         |
| Lime water, or any calcareous waters. | { Deepen the colour.                            |
| Baryta water.                         | { Beautiful yellow flocculent precipitate.      |
| Nitric acid.                          | { Deepens the colour, but gives no precipitate. |

|                       |   |
|-----------------------|---|
| Other acids.          | Render the liquid turbid.   |
| Alum.                 | Slight yellow precipitate.  |
| Protochloride of tin. | Abundant yellow precipitate.  |
| Acetate of lead       | Abundant yellow precipitate.  |
| Ferric sulphate       | { Olive-brown coloration, and, on standing, a brown precipitate.  |
| Acetate of copper.    |   |
| Gelatin.              | Yellowish brown precipitate.  |
|                       | Renders the liquor slightly turbid.   |
| Chlorine.             | { Changes the colour of the liquid to brown and gives a flocculent precipitate; excess of the reagent partially decolorises the liquid. |
| Potassiumdichromate   |   |
|                       | { Acts like the alkalis, then gives a precipitate in yellow plates.   |

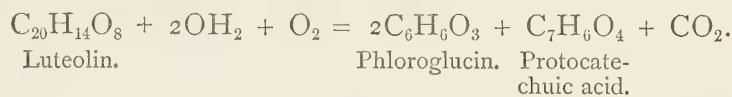
Chevreul, who was the first to isolate the colouring matter of weld, obtained it in pale yellow needles, to which he gave the name *luteolin*. Moldenhauer, who studied it some years afterwards, found its formula to be  $C_{20}H_{14}O_8$ .

Schützenberger and Paraf\* give the following interesting and novel process for the preparation of pure luteolin. The upper part of the weld plant is cut into small pieces and treated with alcohol in a displacement apparatus. The solution thus obtained is concentrated, and on the addition of water greenish flocks are deposited, which are collected and placed with water in a glass cylinder fitting tightly in a strong steel tube firmly closed. It is then subjected to a temperature of 480° F. for twenty minutes and allowed to cool. On opening the cylinder the whole of the upper portion is found to be lined with brilliant golden-yellow crystals of luteolin, whilst a thick resinous cake remains at the bottom. It is necessary to submit the crystals thus obtained to a second treatment, in order to obtain them quite pure. Pure luteolin crystallises in quadrangular needles, which have an astringent, bitter taste. It sublimes

\*Schützenberger, *Traité des Matières Colorante*, ii., 457.

with partial decomposition at a temperature of 600° F. It is freely soluble in alcohol, sparingly so in ether, and but very slightly soluble in hot water. Perchloride of iron imparts a green colour to its solution, even when very dilute. By the action of oxidising agents, such as bichromate of potash, it assumes a magnificent yellow colour similar to that produced on woollen fabrics. Luteolin is not decomposed when boiled with dilute sulphuric acid, and is therefore not a glucoside.

Hlasiwetz and Pfaundler consider luteolin to be an isomeride of paradatiscetin. Rochleder and Brever,\* who have also examined this colouring principle, state that when fused with caustic potash, phloroglucin and protocatechuic acid are produced. Adopting Moldenhauer's formula for luteolin, the following equation represents the decomposition:—



The introduction of quercitrin and flavin has entirely superseded the use of weld in England, but it is still used to some extent for dyeing woollen goods on the continent, where it is employed with alumina mordants to produce various brilliant shades of yellow, and with a mixture of alumina and iron mordants to dye olive-greens.

ALOES.—This drug is the thickened juice of various species of *Aloë*, a genus of plants belonging to the liliaceous order. The species from which it is most commonly derived are the *Aloë vulgaris* or *sinuta*, *A. socotrina*, *A. spicata*, *A. arborescens*, *A. africana*, and *A. ferox*.

The best sorts of aloes are prepared by boiling down in a copper or cast iron pot the juice which exudes from the leaves, which are cut off for that purpose close to the plant.

There are four principal varieties of aloes known in com-

---

\* Jour. für Prak. Chem., xcix., 433.



merce, namely, Socotrine aloes, Barbadoes aloes, Natal aloes, and Cape aloes.

Socotrine aloes, or, as it is also called, Bombay aloes and Zanzibar aloes, is imported from the east coasts of Africa, and southern Arabia, *via* Bombay, in kegs or in boxes lined with tin. When of good quality it is of a dark reddish-brown, and has an odour recalling that of saffron. If moistened with alcohol, and examined under the microscope, it will be seen to contain a great number of minute crystals. When opaque and liver-coloured, it is sometimes called 'Hepatic aloes,' or 'Liver aloes.'

Barbadoes aloes, made from the *A. vulgaris*, is of a deep brown colour, and when breathed on has an odour somewhat resembling the last-named variety of aloes, but easily distinguishable from it. In thin fragments it is orange-brown, and translucent.

Natal aloes, which has been imported from that place in considerable quantity since 1870, is quite unlike ordinary Cape aloes, and is distinguished by containing a peculiar principle, nataloin. It is of a greyish-brown colour, and very opaque. The aloe which yields it is a large plant, and has not, as yet, been identified with any of the known species.

Cape aloes is produced in largest quantity near Algoa bay, in the Cape Colony, chiefly from the species *Aloë spicata*, *A. africana*, *A. ferox*, and *A. aborescens*; it is known in commerce as *Aloë capensis*. Cape aloes has a brilliant conchoidal fracture, and a peculiar odour by which it may readily be distinguished from the other kinds; it is translucent in small splinters, which are of an amber colour by transmitted, but very dark by reflected light; it yields a pale yellow powder.

Aloes has an intensely bitter flavour, and a strong aromatic odour; it is moderately soluble in cold water, and freely soluble in hot water, alcohol, ether, and essential oils. It

contains three substances, two of which are soluble in water, and form in Barbadoes aloes about 70 per cent. of the mass; the third is insoluble in water.

From the aqueous solution of aloes, Messrs. T. and H. Smith, of Edinburgh, succeeded, in 1850, in isolating a compound, to which they gave the name of *aloïn*. In the process they adopted, Barbadoes aloes is treated with cold water, and evaporated *in vacuo* to the consistence of a syrup; this is allowed to stand out of contact with the air for a few days, when a yellow crystalline mass is deposited. This is collected, pressed, re-dissolved in cold water out of contact with the air, and again evaporated *in vacuo*. The process is repeated a third time, when the *aloïn* crystallises out nearly pure in the form of a straw-yellow crystalline mass, readily soluble in boiling alcohol, from which it is deposited in silky tufts of yellow rhombic plates. According to Tilden,\* *aloïn* may be readily prepared from selected Barbadoes aloes, which should have a bright colour and opaque appearance, by dissolving it in boiling water slightly acidulated with hydrochloric acid, and evaporating the filtered solution to a syrupy consistence. In the course of a few days it deposits a lemon-coloured crystalline mass of *aloïn*, which only requires to be freed from the mother liquor by pressure, and then recrystallised, in order to obtain it in a pure state. *Aloïn*, or *Barbaloïn*, is only slightly soluble in cold water and ether; freely soluble in hot water, alcohol, acetic acid, and alkalis. Its solutions are rapidly oxidised in contact with the air if an alkali be present, assuming a brown colour, especially if heated.

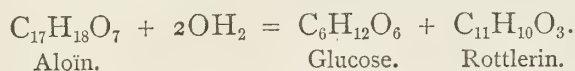
Stenhouse, who in 1850 analysed the product prepared by Messrs. Smith, found that when dried at 212° F. it had the formula  $C_{17}H_{18}O_7$ ; but if dried in *vacuo* at the ordinary temperature it still retained 1 molecule of water of crystallisation. He found also that when *aloïn* in cold aqueous

---

\* Pharm. Jour. [3.] ii., 845.

solution is treated with an excess of bromine, it forms a compound in which three equivalents of hydrogen are replaced by bromine, yielding *bromaloïn*,  $C_{17}H_{15}Br_3O_7$ . This is soluble in boiling alcohol, and separates from the solution on cooling in shining yellow needles, grouped in stars much larger than those of aloïn. It is less soluble in cold water and alcohol than aloïn. Tilden has also prepared the corresponding *chloraloïn*  $C_{17}H_{15}Cl_3O_7$ .

According to Rochleder, aloïn on boiling with dilute sulphuric acid is resolved into glucose and *rottlerin*, the decomposition being



Flückiger\* found that Natal aloes contained a different principle from Barbadoes aloes, which can be readily extracted by treating the drug with its own weight of spirit at a temperature of about 110° F.; this dissolves the amorphous portion and leaves the crystals, which may be purified by pressure and recrystallisation from hot spirit. *Nataloïn*,  $C_{25}H_{28}O_{17}$ , crystallises in thin, bright yellow scales, which are sparingly soluble in absolute alcohol and in ether, more so in methyl alcohol, but only slightly soluble in water. When treated with nitric acid it yields picric and oxalic acids, but no chrysammic acid, showing that it differs essentially from barbaloïn. Histed, whilst examining Socotrine aloes, succeeded in isolating a peculiar principle distinct from both those already described, and which Flückiger, who subsequently investigated the subject, named *Socaloïn*,  $C_{34}H_{38}O_{15} + 5OH_2$ . It crystallises in tufts of acicular prisms, which are much more soluble than nataloïn.

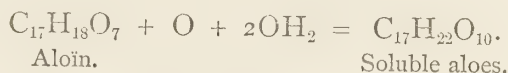
Kosmann,† who experimented on Cape aloes, found that the portion soluble in water and that which is insoluble

\* Arch. Pharm. [2.] cxlix., 11.

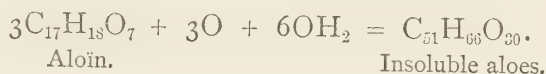
† Bull. Soc. Chem., 1863, p. 530



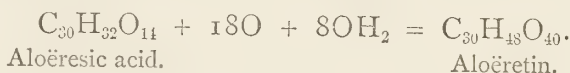
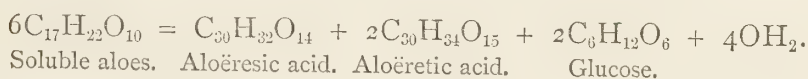
both had the same percentage composition. The soluble compound is a yellow amorphous mass, composed of agglomerated granules, which he supposes to be an oxidised product of aloïn formed during the concentration of the sap, thus:—



The compound insoluble in water is formed in a similar manner:—



On being boiled with sulphuric acid these bodies yield glucose, and various acids of a yellowish-brown colour possessing but little interest,



According to Hlasiwetz, when aloes is boiled with dilute sulphuric acid *paracoumaric acid*,  $\text{C}_9\text{H}_8\text{O}_3$  is obtained, which, by fusion with potash, is converted into *paraoxybenzoic acid*,  $\text{C}_7\text{H}_6\text{O}_3$ . When either aloes or barbaloïn is fused with potassium hydrate it yields the last mentioned acid, and also orcin, the colour-giving principle of the lichens (p. 233).

Schunck, who many years ago studied the action of nitric acid on the aloïn from Barbadoes aloes, found that it gave rise to two compounds, which he named *aloëtic acid*, and *chrysammic acid*, respectively.

To prepare aloëtic acid, one part of aloes is heated with eight parts of nitric acid of 1.3 specific gravity; as soon as the violent oxidising action which ensues is terminated, the solution is concentrated, and water added, when it yields on cooling a yellow powder, which is a mixture of impure aloëtic and chrysammic acids. This is washed with cold water, and treated with boiling alcohol, which dissolves only

the aloetic acid ; on cooling, the alcoholic solution deposits the acid in the form of an orange-yellow crystalline powder.

According to Finck,\* however, the best method of separating the acids is to convert them into potassium salts, and then to treat the mixture with cold water, which dissolves only the aloetate. The solution when mixed with barium acetate and evaporated, yields crystals of barium aloetate, from which, after purification, the aloetic acid may be separated by means of nitric acid.

Aloetic acid  $C_{14}H_4(NO_2)_4O_2$ , is only slightly soluble in cold water, but freely so in hot water and in alcohol. It is soluble in alkalis with a red colour, whilst with ammonia it forms an amide having a violet colour. By long continued boiling with nitric acid, it is oxidised and converted into chrysammic acid. The alkaline aloetates are soluble and crystalline, those of the heavy metallic oxides are insoluble.

*Chrysammic acid*,  $C_{14}H_4(NO_2)_4O_4$ , is obtained by digesting aloes with nitric acid, specific gravity 1.35 (nine parts) until all action ceases, distilling off most of the nitric acid, and after washing the residue with a small quantity of water, digesting it for six or eight hours with an equal weight of nitric acid of specific gravity 1.45. It is then thrown into water, and the yellow flocculent precipitate collected and washed with boiling water until the water passing through assumes a purple colour. Tilden (*loc. cit.*) prefers to prepare it from barbaloin itself, which by the action of cold fuming nitric acid is converted into a mixture of chrysammic, aloetic, oxalic, and picric acids. After washing the product with cold water, which removes the two last mentioned acids, it is boiled with fuming nitric acid for a considerable time, in order to convert the aloetic into chrysammic acid. The crude acid obtained by either of these processes is purified by converting it into the potassium, or calcium salt, and recrystallising. On adding

---

\*Ann Chem. Pharm., cxxxiv., 236.

dilute nitric acid to a solution of the chrysammate, the pure acid is precipitated in the form of golden-yellow scales which are nearly insoluble in water, but impart to it a fine purple colour. It is freely soluble in ether. According to De la Rue and Müller, chrysammic acid is also produced by the action of nitric acid on chrysophannic acid.

The *alkaline chrysammates* are deep red, and crystallise in plates having a golden-green metallic lustre, which are sparingly soluble in cold water. The calcium, barium, and magnesium salts are only very sparingly soluble in water, but more readily in dilute alcohol. They all crystallise well, especially the magnesium compound, which forms large scales of a magnificent crimson colour.

Chrysammic acid, when treated with ammonia, yields *ammonium chrysamidate*  $C_{14}H_2(NO_2)_4O_3(NH_2)NH_4$ , crystallising in dark red needles having a green iridescence. Dilute acids remove the base from this salt leaving free *chrysamidic acid*,  $C_{14}H_2(NO_2)_4O_3(NH_2)H$ .

*Hydrochrysamide*,  $C_{14}H_{10}N_4O_6$ , or  $C_{14}H_4(NH_2)_3(NO_2)O_4$ , a substance crystallising in needles of a fine blue colour, is readily produced from chrysammic acid by the action of reducing agents, such as hydriodic acid, or zinc and dilute sulphuric acid. It is insoluble in water, and only sparingly soluble in boiling alcohol.

Boutin, Robiquet, and especially Saac and Schlumberger, have shown that from aloes, and its derivative chrysammic acid, a great variety of colours may be obtained, including purples, pinks, orange, yellow, chocolate, brown, olive, and grey, which dye both cotton, wool, and silk. The shades given, however, vary considerably on the different fabrics, even when the same mordant is applied; as an instance of this, with an alumina mordant it gives a pearl-grey on cotton, and a yellowish-brown on wool.

**TURMERIC OR INDIAN SAFFRON.**—This is the tuber or underground stem of the *Curcuma tinctoria*, or *longa*, a



plant which grows abundantly in the East Indies. It is also imported from China, Java, Batavia, and Barbadoes, but that shipped from Bombay is the most valued. The roots externally are of a colour inclining to grey, but internally of a deep yellow; they have an aromatic and bitter flavour.

According to John their composition is as follows:—

|  |                 |
|--|-----------------|
| Yellowish volatile oil .....                       | 1               |
| Yellowish-brown resin .....                        | 10 to 11        |
| Brown extractive matter, with dyeing properties    | 11 to 12        |
| Gummy matter .....                                 | 14              |
| Matter soluble in alkalis, including earthy salts. | 57              |
| Moisture, loss, &c. ....                           | 7 to 5          |
|  | <hr/> 100 <hr/> |

Turmeric is ground and sold to the dyers in the state of a fine powder of a remarkably brilliant orange hue, and having a strong odour. It only yields a small amount of colouring matter to cold water; boiling water, however, extracts a larger quantity, whilst alcohol dissolves the colouring matter freely, and at the same time takes up the greater part of the resin.

Vogel and Pelletier were the first to isolate the colouring principle, and gave it the name of *curcumin*; but Lepage afterwards devised a better process for extracting it. The ground roots, after being treated with bisulphide of carbon to remove the volatile oil and resinous matters, are extracted with a weak alkaline solution, which dissolves the curcumin. The alkaline solution is then neutralised with an acid, and the precipitated curcumin is collected, dried, and crystallised from ether. In this state it forms small brown scales, which yield on trituration a brilliant yellow powder. The curcumin may also be extracted from the root by benzene,\* and the crystals purified by dissolving

\* Daube. Deut. Chem. Ges. Ber., iii., 609.

them in spirit, precipitating with basic lead acetate, and decomposing the lead compound with sulphuretted hydrogen. When recrystallised from boiling alcohol it is quite pure, and then forms shining prisms, which are pale yellow by transmitted, and red by reflected light. It is only slightly soluble in water or benzene, even when boiling, but is very readily soluble in alcohol and ether. It gives with alkalis reddish-brown solutions, and is so easily affected by mere traces of free alkali that paper prepared with it is often used to detect their presence. Curcumin,  $C_{10}H_{10}O_3$ , fuses without decomposition at  $229^\circ F$ . It is oxidised by nitric acid with formation of oxalic acid.

It is well known to chemists, that when a piece of turmeric paper is dipped into a solution of boracic acid, it assumes a bright orange colour, which becomes red on the addition of a strong mineral acid such as sulphuric or hydrochloric. This red gradually becomes of a dark purple, especially if the paper be dried. If the same paper be washed, and then dipped into alkaline solutions, it assumes a brilliant blue colour which, however, soon disappears, changing to grey.

Schlumberger,\* who studied this reaction, has obtained some very curious results. If an alcoholic solution of curcumin is boiled with boracic acid, the solution becomes orange, and when cold gives a bright vermilion-coloured precipitate on the addition of water. This precipitate is insoluble in ether and benzene, but is very soluble in alcohol, to which it communicates an orange colour. This compound is very unstable, it decomposes immediately if the alcoholic solution is boiled, or even at ordinary temperatures if kept some time, into boracic acid and a yellow resin, *pseudocurcumin*, which differs entirely from curcumin, giving with alkalis a greenish-grey colour. The compound produced from curcumin by boracic acid dissolves in alkalis

---

\* Bull. Soc. Chim. [2.] v. 192.

with a purple-violet colour, which rapidly changes to a dirty grey.

The most interesting substance, however, obtained by Schlumberger is *rosocyanin*, the alcoholic solution of which has a brilliant rose colour, similar to that of magenta, and which changes to a rich dark blue on the addition of a little ammonia or fixed alkali. It is prepared by treating an alcoholic solution of curcumin with boracic and sulphuric acids. The mixture rapidly acquires a deep red colour, and the operation is completed when, on testing a small quantity of the liquid, it becomes blue on the addition of ammonia. On allowing the solution to cool, the impure rosocyanin crystallises out. When pure, it forms dark red needles with a green iridescence, which are insoluble in water, ether, and benzene. The intense rose colour of the alcoholic solution is rapidly changed by heating, first to a dark red, then orange, and finally yellow. The same change takes place in the cold, but more slowly. Ammonia, as already stated, changes the colour to dark blue, but when the alkali is neutralised the original colour is restored. The blue solution gives blue precipitates with lime and baryta water, but if left in contact with the atmosphere it rapidly becomes grey.

From these experiments it would appear probable that curcumin is a glucoside which combines directly with boracic acid, but which is decomposed by the action of sulphuric acid. Schützenberger remarks that *rosocyanin* has a very great resemblance in its chemical properties to cyanin, the colouring matter of flowers already noticed.

The Chinese dye silk with turmeric by merely dipping the fabric in a decoction of the colouring matter acidulated with citric acid; but although it gives colours with mordants on cotton, silk, and wool, it is not employed as a dyestuff in Europe on account of its fugitive character, except as a constituent of certain compound colours,



especially those known as 'sour browns.' It is used, however, by paper stainers, and to dye wood and leather; also for colouring pastry, butter, cheese, and pomades. It is an important ingredient of the curry powder so largely used in India in cookery.

ANNATTO.—This is the pulpy part of the seeds of the *Bixia orellana*, which grows in South America, and is imported into this country from Mexico, Brazil, the Antilles, and especially from Cayenne, in masses varying in weight from 5 to 20 lbs., which are usually covered with banyan leaves or reeds. It is also imported as a homogeneous paste, in casks weighing 4 or 5 cwt. The paste has the consistence of butter, and often has a repulsive odour of urine, which, it is stated, is added by those who store it, to keep it moist, and to impart to it a richer hue.

At Cayenne, when the fruit of the bixia is ripe, it is gathered, coarsely crushed, and thrown into water, where it remains for several weeks. By this means the pulpy matter is separated from the kernel. It is next strained through a coarse cloth, and the colouring matter gradually subsides. It is then collected, and the excess of water evaporated until it assumes a pasty state, when it is exposed to the atmosphere, in the shade, until sufficiently dry to be shipped. The powder so prepared, and especially at Cayenne, is comparatively inferior, owing to the mass fermenting and producing matters which are injurious in the dyeing process. The following analysis may be taken as the average composition of such qualities of annatto :—

|                                     |        |
|-------------------------------------|--------|
| Water.....                          | 72·25  |
| Leaves .....                        | 3·85   |
| Starch, mucilage, woody fibre ..... | 18·30  |
| Colouring matter .....              | 5·60   |
|                                     | <hr/>  |
|                                     | 100·00 |
|                                     | <hr/>  |

Some forty years ago, M. du Montel introduced at Cayenne some marked improvements in the manufacture of annatto. Instead of crushing the seeds, he washed them with water, so as to separate the colouring-matter, and prevented the fermentation by the addition of some chemical substance. By this means he obtained annatto in a minute state of division, known as bixin, and having a very beautiful red colour, which is imported into this country in the form of small tablets, which are much used for colouring cheese; its dyeing power is, according to Girardin, about three times greater than that of ordinary annatto.

Annatto is only partially soluble in water, but is freely so in ether and alcohol. Hydrochloric and acetic acids have little or no action upon it, but it gives a blue coloration with concentrated sulphuric acid which gradually becomes green, and then violet. It dissolves readily in alkalis and their carbonates, forming a dark red solution in which acids produce an orange-red precipitate.

An alkaline solution of annatto gives an orange precipitate with alum or sulphate of protoxide of iron; a yellowish-brown precipitate with salts of copper; and a lemon-coloured precipitate with chloride of tin.

Common annatto, although sold at a comparatively low price, is an expensive colouring matter, owing to the small amount of colour-giving principle which it contains, even when unadulterated. It is often, however, mixed with ochre, and other coloured earths. To detect this fraud, it is only necessary to dry it and calcine it, when, if pure, it will not leave more than 8 to 12 per cent. of ash on the dried annatto. The best process, however, to determine the dyeing power, is to dye equal weights of cloth with a sample of the annatto to be tested, and with one of known good quality. The bath should be composed as follows:—

|                               | FOR COTTON. | FOR SILK. |
|-------------------------------|-------------|-----------|
| Annatto, dried at 212° F. ... | 75 grains   | 7.5       |
| Cream of tartar .....         | 150 „       | 15.0      |
| Water .....                   | 6,000 „     | 3,000     |

Two hundred grains of cotton yarn, and 30 grains of boiled silk, are then weighed and immersed in their respective baths, the whole boiled for fifteen minutes, and left to cool for an hour. The dyed samples are then taken out, squeezed, washed thoroughly, and dried in diffused daylight, and the intensity and brilliancy of the two samples compared. The comparative value of two samples of annatto may also be approximately determined by the colorometer. To prepare the solutions for this purpose, 7 grains of each sample are digested in 700 grains of alcohol, of 90 per cent., this liquid is then poured off, and the operation repeated seven times. The intensity of colour of the alcoholic extract from the two samples is compared.

The colouring matters of annatto have been studied by Chevreul, Kerndt, Picard, Bolley, Mylius and Stein. It contains two colouring matters, one of which, *orellin*, is yellow, soluble in water and alcohol but insoluble in ether; it gives a yellow colour to cloth mordanted with alum. Kerndt considers it to be a product of the oxidation or decomposition of the second colouring principle, *bixin*, to which Bolley assigns the formula  $C_5H_6O_2$ ; Stein, however, considers it to be  $C_{15}H_{18}O_4$ . Bolley and Mylius state that neither Kerndt nor Picard obtained pure bixin, but a mixture of that body with a resinous substance. To prepare it, the best quality of annatto from Cayenne, after having been washed and dried, is boiled with concentrated alcohol; the alcoholic solution is evaporated to dryness, and placed to digest with ether, which dissolves a part of the residue, leaving a bright red powder, insoluble in water. This is dissolved in alcohol, and an alcoholic solution of acetate of lead added to it, when a red lake is produced, which is



washed with alcohol, suspended in water, and decomposed by sulphuretted hydrogen. The red colouring matter is removed from the lead sulphide by boiling it with alcohol, which, on concentration, and the addition of water, yields a red flocculent precipitate of bixin. When dried, it is a Cinnabar red powder, insoluble in water or ether, but soluble in alcohol and benzene. It is readily soluble in alkaline solutions, and is coloured dark blue by concentrated sulphuric acid.

The use of annatto in print and dyeworks is rather limited, being chiefly employed to modify the shades of other dyes, such as certain tints of yellow produced by fustic or quercitron. It is also used to give a bottom to cotton before it is dyed with safflower or cochineal. In the production of oranges in steam styles, annatto is now entirely superseded by *aurin*, a colour derived from carbolic acid. It is still often used in dyeing a low class of cotton yarns; the yarns being dipped in an alkaline solution of annatto, and then passed through dilute sulphuric acid, which precipitates the bixin in the fibre. It is then only necessary to wash the cotton to complete the operation. If an orange-yellow tint is required, the cotton is previously mordanted with tin.

It is often employed to colour varnishes, cheese, and butter. It is used also by the American Indians and Caribs to dye their bodies.

CHICA OR CARAJARA.—This is an orange-red colouring matter obtained by the Indians from the leaves of the *Bignonia chica*, which grows on the banks of the Rio Meta and the Orinoco, and is employed by them, like annatto, to dye their bodies. It is also used in the United States to produce red and orange shades on cotton and wool, the process followed being similar to that for annatto.

To prepare the colouring matter, the Indians boil the leaves for some time in water, then throw the whole on a

strainer, and add some of the bark of a tree known as 'aryane', which causes a red flocculent matter to be deposited on standing. This is collected, made into cakes, and dried. These cakes have an orange-red colour, are inodorous and tasteless, and acquire a coppery lustre by friction.

The colouring principle is insoluble in water, but is soluble in alcohol and ether, to which it imparts a fine ruby-red colour. Acetic and hydrochloric acids dissolve it, acquiring a reddish-brown tint, whilst with sulphuric acid it gives an orange colour which changes to a dark purple on the addition of ammonia. Caustic and carbonated alkalis, and ammonia dissolve it, forming orange-red solutions, from which it is again separated on the addition of an acid.

Erdmann has examined the colouring principle, to which he assigns the formula  $C_8H_8O_3$ .

SAFFRON.—*Saffron*, the stigmata of the flower of the *Crocus sativus* is obtained from Austria, Spain, and France, especially in the neighbourhood of Avignon. The stigmata are gathered in October, and dried in the sun or over a slow fire. It requires 100,000 stigmata to produce a pound of saffron, which explains why it is such an expensive drug. It has a rather agreeable odour, and a bitter, pungent taste. It yields to water and alcohol, a yellow colouring matter called saffronin, but which is now seldom used as a dye, although formerly a favourite one. *Saffronin*, or *crocin*, may be obtained as an inodorous pink powder, which becomes brown when heated, and is decomposed at  $400^\circ$  F. It yields an orange-coloured solution with water, alcohol, and the alkalis, but is nearly insoluble in ether. Concentrated sulphuric acid dissolves crocin, becoming first blue, and then purple. Boiling with dilute sulphuric acid causes it to split up into glucose, and a dark red amorphous body called *crocin*, having the formula  $C_{20}H_{26}O_{11}$ .

BARBERRY ROOT.—This is the root of the *Berberis vulgaris*, or common barberry, which grows in nearly

all parts of the world, but perhaps most luxuriantly in India.

The colouring principle, *berberine*, was first isolated by Buchner.\* To prepare it, the root is exhausted with boiling water, the extract concentrated by evaporation, and then treated with hot alcohol; after filtration the greater part of the alcohol is distilled off, and the residue left to itself in a cool place; yellow crystals of berberine are then deposited, and may be purified by recrystallisation, first from water, and then from alcohol.

The best method of extracting the berberine† from those sources, such as barberry bark and colombo wood, which do not contain much starch, is to boil them with water and a slight excess of basic lead acetate, filter and concentrate until the substance crystallises out on cooling. After the crystals have been collected, the remainder of the alkaloid is precipitated from the mother liquors as nitrate by the addition of excess of nitric acid. The free base can be obtained from the nitrate by heating its aqueous solution with milk of lime. In order to purify the crude berberine, it is dissolved in boiling water, basic acetate of lead added as long as a precipitate is produced, the solution filtered, and the excess of lead removed by means of sulphuretted hydrogen. On cooling, pure berberine crystallises out.

Berberine has also been found in *Berberis aristata*; in *Fateorhiza palmata* or *Cocculus palmatus*, the calumbo, or colombo root, by Bödeker;‡ in the colombo wood of Ceylon, *Menispermum fenestratum*, by Perrins;§ by Stenhouse|| in 'yellow bark', *Coelocline polycarpa*, used as a dye by the natives of Abeocouta in West Africa;

---

\* Ann. Chim. Pharm., xxiv., 228.

† Jour. Chim. Soc., xx., 187.

‡ Ann. Chim. Pharm., lvi., 384, and lxix., 40.

§ Ibid., lxxxiii., 276.

|| Pharm. J. Trans., xiv., 455.



by Mayer\* in podophyllum root, *Podophyllum peltatum*, and from the root of the *Hydrastis canadensis*. It forms yellow silky needles which have a strong bitter taste. It is only sparingly soluble in cold water or alcohol, but freely so when boiling; it is insoluble in ether, but the fixed and volatile oils dissolve it to a slight extent. Berberine is an alkaloid of the formula  $C_{20}H_{17}NO_4$ , which in alcoholic solution gives green lustrous scales, with solution of iodine or iodide of potassium. It combines with acids, yielding well defined yellow-coloured salts, of which the nitrate is remarkable for its insolubility in solutions containing a slight excess of the acid; it is decomposed by boiling nitric acid, yielding oxalic acid among other products. Nascent hydrogen converts it into a colourless compound, *hydroberberin*,  $C_{20}H_{21}NO_4$ . Barberry root has been used alone to dye silk yellow, but alum and salts of tin brighten the colour. Its chief use, however, is for dyeing leather.

GAMBOGE.—This is a gum-resin, produced from the *Garcinia morella*, a tree belonging to the order *Guttiferæ*, and growing in the peninsula of Camboga, in Siam, and in the southern parts of Cochin China. A yellow juice flows from incisions made in the trunk of the tree, which is collected in bamboos, and allowed to thicken, when it forms cylinders, often streaked with impressions from the inside of the bamboo. This is the finest sort, called the *pipe gamboge* of Siam. A portion is also formed into round cakes, either entire, or having a hole in the middle. Gamboge is also produced in Ceylon; and an inferior sort is said to be obtained from the *Gambogia gutta*; a tree growing wild on the Malabar coast.

Gamboge occurs in pieces of various sizes, of a dirty-yellowish colour externally, and covered with a yellow powder. When broken, it exhibits a vitreous or conchoidal

---

\* Amer. Jour. Pharm., xxxv., 97.

fracture, with brown or saffron-yellow colour. Its powder is of a brilliant yellow, and forms an emulsion with water. Although it is nearly without odour at ordinary temperatures, it gives out a very peculiar one when heated. When taken into the mouth, it has at first scarcely any perceptible taste, but after a time it causes a sharp, acrid sensation in the throat. It is a drastic purgative.

Gamboge dissolves in alcohol, in ether, and in ammonia. The ammoniacal solution forms a red precipitate with salts of barium; yellow with zinc salts; reddish-yellow with acetate of lead; and brownish-yellow with nitrate of silver.

The following analyses of gamboge are by Dr. Christison.

|                        | PIPE GAMBOGE,<br>FROM SIAM. |       | CAKE GAMBOGE,<br>FROM SIAM. |       | CEYLON GAMBOGE. |       |       |       |
|------------------------|-----------------------------|-------|-----------------------------|-------|-----------------|-------|-------|-------|
| Resin .....            | 74.2                        | 71.6  | 64.3                        | 65.0  | 68.8            | 71.5  | 72.9  | 75.5  |
| Gum .....              | 21.8                        | 24.0  | 20.7                        | 19.7  | 20.7            | 18.8  | 19.4  | 18.4  |
| Amylaceous<br>matter } | .....                       |       | 6.2                         | 5.0   | .....           |       | ..... |       |
| Woody fibre .....      |                             |       | 4.4                         | 6.2   | 6.8             | 5.7   | 4.3   | 6     |
| Moisture ...           | 4.8                         | 4.8   | 4.0                         | 4.6   | 4.6             | ...   | ...   | 4.8   |
|                        | <hr/>                       | <hr/> | <hr/>                       | <hr/> | <hr/>           | <hr/> | <hr/> | <hr/> |
|                        | 100.8                       | 100.4 | 99.6                        | 100.5 | 100.9           | 96.0  | 96.6  | 99.3  |

The resin contained in gamboge is easily separated by means of ether; it is hyacinth-red, and yields a powder of a fine yellow colour. It possesses marked acid properties, decomposing alkaline carbonates at the boiling heat, and forming with the alkalis red salts, which may be separated from their solutions by common salt, like soaps. Buchner assigns to it the formula  $C_{30}H_{35}O_6$ .

The purified resin, when fused with caustic potash, gives off vapours having a pleasant aromatic odour, and the residue is found to contain phloroglucin, pyrotartaric acid, and two other acids, one of which is crystalline, and the other not. The crystallised acid, which Hlasiwetz and Barth\* call *isouvitic acid*,  $C_9H_8O_4$ , is isomeric with uvitic

\* Ann. Chem. Pharm., cxxxviii., 61.

acid, and forms thick prismatic crystals, belonging to the rhombic system.

The principal use of gamboge is as a pigment in water-colour painting. An imitation gamboge is prepared from turmeric.

ILIXANTHIN.—This is a yellow colouring-matter, first observed by Nachtigal in the leaves of the *Polygonium fagopyrum*, or common buckwheat, and afterwards investigated by Schunck. It appears to be identical with the ilixanthin which Moldenhauer\* obtained from the leaves of the holly *Ilex aquifolium*. It crystallises in pale yellow needles, having the composition  $C_{17}H_{22}O_{11}$ , and which are only sparingly soluble in hot or cold water, but more soluble in alcohol. Strong sulphuric acid changes its colour to a deep yellow, without decomposition. It yields on calico mordanted with alumina, a dark yellow colour; with tin, a light yellow; and with oxide of iron, various shades of yellowish-brown, according to the strength of mordant employed.

LICHENS.—Various yellow-coloured substances have been obtained from the lichens, namely, *chrysophanic acid*, and *vulpic acid* or *chrysopicrin*. Rochelder and Helt obtained *Chrysophanic acid* (see rhubarb, p. 298) from the *wall lichen* or *Parmelia parietina*.

*Vulpic acid*, or *chrysopicrin*, was obtained by Möller and Strecker, from the *Cetraria vulpina*, growing in Norway; by Bolley and Kinkelyn, from the *Evernia vulpina* of the Alps; and by Stein, from the *Parmelia parietina*.

*Chrysinic acid*, prepared by Picard from Poplar buds, appears to bear a very close resemblance to vulpic acid.

To prepare these various yellow acids, the lichens are macerated in an alkaline liquor, which is then separated from the weed, and neutralised with an acid, when the colouring principle separates. It is washed, and dissolved



in alcohol or ether, which, on evaporation, yields the acid in a crystalline state.

*Vulpic acid* crystallises in needles of the formula  $C_{19}H_{14}O_5$ , which dissolve freely in water, alcohol, and ether. It sublimes without decomposition at  $250^{\circ}$  F. and gives a golden-yellow solution with alkalis, which is not changed by exposure to the atmosphere. It produces a good yellow colour as a dye. *Chrysinic acid* possesses very little interest.

PURREE, OR INDIAN YELLOW.—*Purree*, or *Indian yellow*, is a colouring matter imported from India and China in round lumps, weighing from 3 to 4 ozs., of a brown colour externally, and of a bright yellow internally, and, according to Erdmann, exhibiting a crystalline structure. Although, when boiled in a solution of borax, it yields a fine yellow colour on silk and cotton prepared with alumina mordants, it is not employed for that purpose, on account of its high price. Its chief use is as a pigment in oil and water-colour painting.

The origin of this substance is still a disputed question. Some believe it to be an intestinal or biliary concretion of the camel, the elephant, and the buffalo; whilst others think that it is a deposit from the urine of these animals when they have been eating the leaves of certain plants, among which is the mango, or *Mangostana mangifer*.

The colouring matter is magnesium euxanthate, from which the *euxanthic acid* is prepared by washing the purree thoroughly with boiling water, and dissolving the residue in boiling dilute hydrochloric acid, which, on cooling, deposits the euxanthic acid in tufts of yellow needles. It has a sweet taste, and bitter after taste; and is freely soluble in ether and alcohol, but only slightly so in water. Its formula, when crystallised from alcohol, is  $C_{21}H_{18}O_{11} + OH_2$ , but it loses the molecule of water when dried at  $265^{\circ}$  F.

If precipitated from its ammoniacal solution by hydrochloric acid, it retains three molecules of water,  $C_{21}H_{18}O_{11} + 3OH_2$ .

According to Stenhouse, if the anhydrous acid be cautiously heated in a tube, it yields a yellow sublimate, to which he has given the name *euxanthone*,  $C_{20}H_{12}O_6$ .

Euxanthic acid forms well defined salts. Numerous derivatives have also been obtained by the action of various reagents, such as bromine, chlorine, nitric acid, &c., but they are interesting only from a scientific point of view.

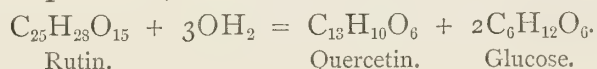
Indian yellow being somewhat costly, is often adulterated with cheaper yellows, such as chromate of lead. This may be detected by calcination, when the genuine yellow undergoes slow combustion, leaving only a small amount of ash, whilst if mineral matter has been added a larger percentage will be found.

**RHUBARB.**—This drug, which is the root of various species of *Rheum*, as *R. palmatum*, *R. compactum*, *R. australe*, &c., contains several definite chemical compounds, the most important of which is *chrysophanic acid*. This is best extracted from the root by exhausting it with cold water, drying it, and boiling it with benzene. On concentrating the benzene solution by distillation, and allowing the residue to cool, it solidifies to a crystalline mass of the acid, which may readily be purified by treating it with a dilute solution of soda, and recrystallisation. Chrysophanic acid crystallises in pale yellow, six-sided plates, which are almost insoluble in water, and but slightly soluble in alcohol. It is not as yet definitely settled whether its formula is  $C_{14}H_{10}O_4$ , or  $C_{14}H_8O_4$ . When boiled with fuming nitric acid it is converted into chrysammic acid (p. 283). Chrysophanic acid also exists in senna, in *Rumex obtusifolius*, and many other species of this genus, and also in *Parmelia parietina*, the yellow wall lichen.

**RUTIN.**—*Rutin* is a glucoside which appears to be widely diffused in the vegetable kingdom. It was first obtained

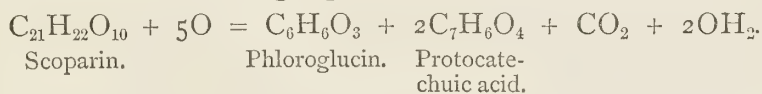
from garden rue by Weiss and Bornträger, afterwards from capers by Rochleder and Hlasiwetz, and by Stein from Waifa, the undeveloped flower buds of the *Sophora japonica*. It crystallises from its aqueous solution in pale yellow crystals, to which the formula  $2C_{25}H_{28}O_{15}, 5OH_2$  has been assigned. It loses three molecules of water at  $212^{\circ} F.$ , and the remaining two at  $320^{\circ} F.$  It is nearly insoluble in cold water, but freely soluble in boiling water, or hot alcohol; it is insoluble in ether, but soluble in acetic acid. It dissolves freely in alkalis, and their carbonates; and also in lime, and baryta water, forming yellow solutions from which acids precipitate the rutin unaltered. These solutions become brown on exposure to the atmosphere.

Cold nitric acid at first imparts a yellow colour to rutin, which quickly passes to an olive, and finally to a brown. Boiling nitric acid converts it into oxalic and picric acids. Boiled with dilute sulphuric acid, rutin is decomposed into glucose and quercetin, as shown in the following equation:—



When acted on by sodium-amalgam, rutin yields *paracarthamin*.

SCOPARIN,  $C_{21}H_{22}O_{10}$ .—This compound which was obtained by Stenhouse from the *Spartium scoparium*, although not a dyestuff, is considered by Hlasiwetz to belong to the quercetin group, for when fused with caustic potash it is split up into phloroglucin and protocatechuic acid, as represented in the following equation:—



Scoparin, when freed from chlorophyll and other impurities, is a pale yellow, brittle, amorphous mass, which may, however, be obtained in small crystals by the spontaneous evaporation of its alcoholic solution. It is a neutral compound, and is tasteless and inodorous: with alkalis



and their carbonates, or with ammonia, it gives yellowish-green solutions. The ammoniacal solution leaves on evaporation a green jelly, which, when dry, is free from ammonia, and has the same composition as the crystallised body. Scoparin, in fact, readily assumes either the colloid, or the crystalline form.

TAIGU, OR TAYEGU WOOD.—M. J. Arnaudon,\* some years ago, on examining with a microscope a sample of *Taigu wood* imported from Paraguay, observed some yellow prismatic crystals, which proved to be a colouring matter. To extract it, the wood is cut into small pieces and treated at the ordinary temperature with alcohol of '844, which dissolves the colouring principle together with a little reddish-brown resin. This alcoholic solution, when concentrated, yields crystals of the impure colouring matter, which may be purified by recrystallisation, first from alcohol, and afterwards by the spontaneous evaporation of the ethereal solution. The new substance, *taiguic acid*, forms golden-yellow prisms, which are not altered by exposure to the air if light be excluded, but in sunlight it becomes orange-coloured, and finally brown. It melts without decomposition at 275° F., and sublimes at 356° F., yielding large prismatic crystals. As already noticed it is soluble in alcohol and ether, but insoluble in water. It dissolves also in wood spirit and bisulphide of carbon. It is soluble in alkaline solutions with intense scarlet colour, so that it forms a very delicate test for the presence of free alkali. If a small quantity of taiguic acid be added to water containing a millionth part of free ammonia, a distinct coloration is perceptible.

A decoction of taigu wood made with alkaline carbonates imparts a fine orange-red colour to cotton, dipped first into the solution, and then into a bath of dilute acid. The dye is very similar in shade to that obtained with annatto.

---

\* Technologiste, xix., 453.

WONGSHY, OR HOANG-TCHY.—Rondot, Persoz, and Martius, have examined four yellow colouring matters employed in China, but of these only one, called *Wongshy*, or *hoang-tchy*, and which is the fruit of the *Gardenia grandiflora*, appears to possess any peculiar interest.

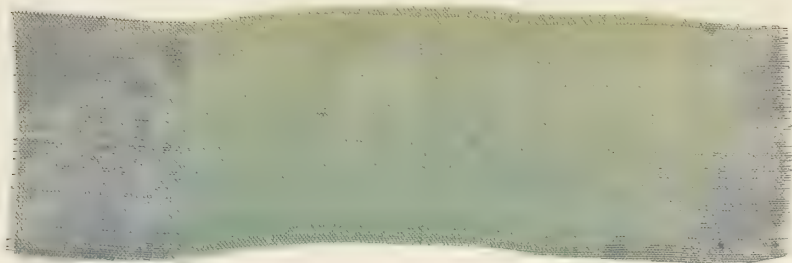
The colouring principle has been studied by Stein, Orth, Rochleder, and Martius, and according to Rochleder is identical with crocin, the colouring matter of saffron.

CAROTIN.—The yellow colouring matters of carrots, gentian root, and several other plants have been studied, but present no special interest as they have received no applications.

ROTTLERA.—The fruit of the *Rottlera tinctoria* is used in India for dyeing silk an orange colour. It contains a principle, *rottlerin*, having the formula  $C_{11}H_{10}O_3$ , which crystallises in yellow silky needles; they are insoluble in water, but moderately soluble in ether and in boiling alcohol.

#### GREEN COLOURING MATTERS.

LO-KAO, OR CHINESE GREEN.—In 1848, attention was drawn by several English gentlemen to samples of a green colouring matter coming from China, which in the mean time was studied in France by Kœchlin, Schouch, and Persoz. In 1853, MM. Guinon, Marnas, and Co., of Lyons, imported it in sufficient quantity to enable them to dye silk for the requirements of trade. The silks so dyed were known by the names of *Vert-venus*, *Vert-azof*, *Vert-lumiere*, and were specially admired from their retaining their green colour when seen by artificial light. We are indebted to the kindness of Messrs. Guinon, Marnas, and Co., of Lyons, for the accompanying specimen of the effect obtained on silk with lo-kao.



LO-KAO.

The use of this colour was, however, discontinued, as it was not very fast, and Messrs. Guinon, Marnas, and Co., found that they could produce greens possessing the same property by first dyeing their silks with Prussian blue, and then in an acidulated bath of picric acid. It is interesting to observe that if indigo be substituted for Prussian blue, the colour appears blue by artificial light. This process has since been superseded by the beautiful aniline greens.

M. Charvin, of Lyons, received a gold medal from the Chamber of Commerce of Lyons, for the discovery of a process for preparing lo-kao from a plant indigenous to Europe—the *Rhamnus catharticus*, or buckthorn.

According to Persoz, the lo-kao imported into this country had three shades of a dark greenish blue, and had the following composition :—

|                                    |        |
|------------------------------------|--------|
| Colouring matter.....              | 61·90  |
| Mineral matter, chiefly lime ..... | 28·80  |
| Water .....                        | 9·30   |
|                                    | <hr/>  |
|                                    | 100·00 |

It is insoluble in alcohol, ether, and bisulphide of carbon, and only partially soluble in water. The addition of an acid increases its solubility. The alkalis dissolve out of it a green colouring matter, and the solution becomes brown on being boiled, or even if kept for some time at ordinary temperatures.

Reducing agents such as arsenious, hyposulphurous, oxalic,



and formic acids, give rise to a violet-purple precipitate with lo-kao, whilst sulphuretted hydrogen imparts to it a blood-red coloration. Exposure to the atmosphere restores after a time the green colour. Protochloride of tin dissolves it partially with an intense red coloration, which changes to green on the addition of an alkali and exposure to the air. Oxidising agents, such as nitric and chromic acids, also convert the green colour into a red one; but in this case the green colour is not restored by exposure to the air. Certain salts, such as those of magnesia and zinc, change the green colour to blue. Cloëz and Guignet have recently published a paper on this interesting substance, in which they state that if lo-kao is mixed with water, and left in a warm place for several days, it ferments and becomes partially reduced. If it be now washed with cold water and then boiled in that menstruum, a reddish-violet coloured solution is obtained, which gives a blue precipitate when exposed to the atmosphere. This compound they, in common with Persoz, consider to be the true colouring principle of lo-kao, and have named it *lokain*. It may be prepared in larger quantities by agitating the lo-kao with a solution of carbonate of ammonia, filtering, and precipitating with alcohol.

To obtain pure lokain, one part of pure carbonate of ammonia is dissolved in forty parts of water, and one part of roughly powdered lo-kao added, the mixture being shaken from time to time for about four days, when the liquor assumes a very dark greenish-blue colour. The solution thus obtained is filtered and evaporated to dryness in a water bath, to drive off the excess of ammonium carbonate. The residue, which is soluble in water, is a combination of lokain with ammonia, and is further purified by dissolving it in water and precipitation with alcohol. On analysis it yields numbers corresponding to the formula  $C_{28}H_{33}O_{17},NH_4$ . This compound, on being kept at a tem-

perature of  $212^{\circ}$  F. for several hours, is decomposed, and yields *ammonium lokaetin*, an insoluble violet-coloured substance. The same substance is produced when lo-kao is fermented with the addition of yeast: the solution assumes an intense red colour, and on filtration and exposure to the air a rich purple precipitate is thrown down, which is ammonium lokaetin.

By the action of sulphuric acid the solution of ammonium lokaïn is decomposed into glucose and an insoluble substance lokaetin, to which the formula  $C_9H_8O_{10}$  has been assigned. Lokaïn is therefore a glucoside.

Lokaetin assumes a most intense purple in the presence of the slightest trace of alkali. With sulphide of ammonium it gives a red flocculent precipitate. Nitric acid transforms it into oxalic acid and a new yellow colouring matter.

From the various colours which lokaïn gives under the influence of certain chemical reagents, and from its being prepared from a species of *Rhamnus*, it was the author's opinion that there existed a very close analogy between this compound and some of the derivatives of rhamnetin, if not an absolute identity. In all probability, therefore, there must be an intimate relation between it and quercetin, and especially the rosocyanin obtained from turmeric.

The solution obtained by digesting lo-kao with water, dyes silks a pale bluish-grey similar to that observed on some Chinese silks. Ammonium lokaetin alone, dyes cotton, silk, and wool of a violet colour, no mordant being required. If employed in a bath of hyposulphite of soda, it dyes cotton a fast bright sky-blue, which is permanent when exposed to light.

WAIFA.—There have been several other green colouring matters sent from China to Europe, but with the exception of waifa, they have no special interest, their composition and mode of application being unknown.

Waifa is the undeveloped flower-buds of the *Sophora*

*japonica*, which grows abundantly in the southern parts of China, and in India. Stein extracted from it a yellow colouring principle, which he considers to be identical with rutin.

To obtain a green colour, the Chinese dip the cotton to be dyed into a boiling solution of waifa, to which a small quantity of alum has been added, and then expose the fabric to the sun's rays. These operations are repeated until the required depth of shade is obtained.

SAP GREEN.—There has for many years been a green in use prepared from the *Rhamnus catharticus*, or buckthorn, and known by the name of *sap*, or *bladder green*. It is employed by paper stainers and leather dyers, and is largely manufactured in the neighbourhood of Neuremberg. The ripe berries are submitted to pressure, when a purple-red juice is obtained, which becomes green on the addition of an alkali. To produce the colour, a little soda or lime is added, together with a small quantity of alum and gum. The liquid is then concentrated to the state of a thick syrup, and filled into pig bladders; it is from this circumstance that it derives its name of 'bladder green.'

CHLOROPHYLL.—Notwithstanding the numerous researches which have been made by some of the most distinguished chemists on the green colouring matter of leaves, we are still far from having a correct knowledge of its composition and properties. The great difficulties attendant on the investigation of this subject, are owing, not only to the green colouring principle being associated with various other substances of a waxy or fatty nature, but also to the readiness with which chlorophyll becomes altered by the action of chemical agency, and even by exposure to light.

It may be obtained by the following process:—green leaves are digested several days with ether, and the filtered liquid evaporated to dryness. The residue is treated with boiling alcohol, and a small quantity of milk of lime added



to the solution, which precipitates all the colouring matter, whilst the alcohol retains a quantity of the fat which was mixed with it. The chlorophyll is separated from the lime by means of hydrochloric acid, and ether is then added to dissolve the colouring matter, which forms a green stratum at the top of the liquid.

The chlorophyll is obtained on evaporating the ethereal solution, but not in a pure state, as it is still contaminated by a certain amount of fatty matter.

Hartsenn\* mixes finely chopped ivy leaves with spirit of wine of 55°, and after allowing them to stand twelve hours, presses them: this removes the water, a bitter substance called helicin, and a saponifiable compound. The pressed leaves are now soaked in benzene for twenty-four hours, and the benzene is removed from the expressed solution by distillation. The dark-brown fatty residue, amounting to  $2\frac{1}{2}$  per cent. of the leaves, is treated with a solution of soda, filtered, and precipitated by common salt. The precipitate, after being washed with a salt solution, is dissolved in water, and precipitated with a solution of copper sulphate. This precipitate, after being washed and dried, is boiled with absolute alcohol, and then washed with ether and benzene; this treatment removes the copper soap, and leaves the compound of chlorophyll with copper oxide. On suspending the latter in alcohol, and decomposing it with sulphuretted hydrogen, a solution is obtained, which leaves pure chlorophyll on evaporation.

Chlorophyll, thus prepared, is quite free from fatty matter, and is an earthy powder of a very deep green colour, almost black, unalterable in the air, infusible, sustaining a heat of 390° F. without decomposition, but decomposing at higher temperatures. It is insoluble in water, even at the boiling heat, but is easily soluble in hydrochloric acid, and in alcohol; less so in ether.

---

\* Chem. Centr. 1873, 204.

Among those chemists who have studied the green colouring matters of leaves, M. Fremy\* is of opinion that the green colour is composed of two substances, a yellow and a blue; to the former of which he gives the name *phylloxanthin*, and to the latter *phyllocyanin*. If dried green leaves, or the alcoholic extract from leaves, be agitated with a mixture of ether and dilute hydrochloric acid, and allowed to stand, the liquid separates into two layers; the supernatant ethereal one having a yellow colour, whilst the hydrochloric acid solution has a blue colour. Again, on mixing an alcoholic extract of the leaves with gelatinous alumina, and then carefully adding water, a bright blue lake is precipitated, whilst the solution has a bright yellow colour. If the solution be now filtered, a fresh quantity of hydrate of alumina added, and then a large quantity of water, a yellow precipitate is produced. The lakes thus obtained may be collected, washed, and dried, and if then treated with alcohol, yield to that solvent their respective colours.

Fremy also observed that young and sickly leaves, when exposed to the vapours of hydrochloric acid, assumed a bright green tint, the yellow colouring matter existing in larger quantity than in normal leaves. In the autumn leaves, however, he could find no trace of phyllocyanin, phylloxanthin only being present; the latter is therefore a more stable compound than the former.

*Phylloxanthin*† is a neutral substance, insoluble in water, soluble in alcohol and ether, and crystallising therefrom in yellow laminæ, or red prisms, resembling those of potassium bichromate. It possesses very great colouring power, and dissolves with blue colour in strong sulphuric acid, whereas the yellow colouring matter of flowers becomes red under similar circumstances.

*Phyllocyanin* is insoluble in water, but dissolves with

---

\* Compt. Rend., l., 405.

† Fremy, Ann. Chim. Phys., [4] vii., 78. Ludwig, Arch. Pharm., [2] cvi., 164.

olive-green or bronze-red colour in alcohol and ether; its salts are brown and green; those of the alkali-metals are yellow, and soluble in water. The solutions of phyllocyanin in sulphuric or hydrochloric acid are green, reddish-violet, or blue, according to the degree of concentration; the phyllocyanin being precipitated from them on the addition of water. Alkalis change its colour to bright yellow, but it again becomes green, if it be dissolved in alcohol and hydrochloric acid added.

Professor Stokes \* concludes from the optical characters of chlorophyll, that it is a mixture of four different colouring matters, two of which are yellow, and two green. The solutions of the green (but not of the yellow) colouring matters exhibit strong red fluorescence; three of these substances are very easily decomposed by acids or acid salts, binoxalate of potash for example. Fremy's phyllocyanin is, according to Stokes, merely a product of decomposition of the green bodies by acids; it is soluble in most acids, yielding green or blue solutions. Neutral solutions exhibit very sharp absorption bands. Phylloxanthin varies in its properties according to the manner in which it has been obtained. If the green substances have been removed by means of hydrate of alumina, it is one of the yellow substances existing in the plant; if, however, acids have been used in its preparation, it consists of the same yellow substance, contaminated, however, with the products of the decomposition of the green substance.

According to Filhol,† all the methods of preparing chlorophyll in which acids are used, yield nothing but products of decomposition. By cautious treatment, four substances may be obtained, namely: a yellow compound, soluble in alcohol, which is resolved, by treatment with strong hydrochloric acid, into a blue soluble substance and

---

\* Proc. Roy. Soc., xiii., 144.

† Ann. Chim. Phys., [4] xiv. Compt. Rend., lvi., 1218, and lxi., 371.



a yellow precipitate. On adding oxalic acid to an alcoholic solution of chlorophyll, a brown body is separated: this is soluble in alkaline solutions with an orange-red colour, which, on exposure to the air, becomes pure green from absorption of oxygen.

Lommel,\* who has lately published a paper on the optical properties of chlorophyll, states, that the dark absorption bands observed in a solution of chlorophyll in dilute alcohol, when examined with the spectroscope, correspond, both in position and brightness, with the bright fluorescent bands produced in the same solution. The spectrum of chlorophyll, both when fresh, and after it has become modified by the action of light, has been investigated by Gerland,† and by Chautard.‡

Occasionally, dead trees contains a bright green colouring matter which differs from chlorophyll. It is soluble in chloroform, and is called *xylochloric acid*.

M. Hartmann has succeeded in preparing a pigment from chlorophyll, which, when properly thickened and mixed with lime water, may be printed and steamed in the usual way, yielding colours which are fast, although not bright. The pigment is extracted from grass, which has previously been washed with warm, very dilute lye, by steeping it for twenty-four hours in a solution containing  $7\frac{3}{4}$  per cent. of caustic soda. On neutralising the deeply coloured solution with hydrochloric acid, a green flocculent precipitate is produced, which only requires to be collected on a filter and washed, in order to be ready for use.

---

\* Pogg Ann. cxliii., 568.

† Pogg Ann. cxliii., 585.

‡ Compt. Rend. lxxv., 1837, and lxxvi., 570.

## CHAPTER X.

### TANNIN MATTERS.

There are certain principles widely distributed over the vegetable kingdom which have an astringent taste, and possess the property of giving a blue, or green coloration or precipitate with persalts of iron. These astringent substances, or tannins, as they are called, when added to solutions of gelatin or albumen, produce a precipitate which is a compound of the animal substance with the tannin. All these compounds resist putrefaction in a remarkable degree; those obtained with gelatin forming the basis of leather. It has been known from time immemorial that the skins of animals, and other animal membranes, when steeped for a certain length of time in solutions of these astringent matters, undergo a change by which they are rendered less liable to putrefaction, and available for many purposes of civilised life. The process by which this is effected is called tanning, and those matters which have been found to contain such a proportion of the principles as to be applicable for this purpose have received the name of *tannin matters*. The tannin is contained in various parts of plants; in some cases it is the bark, in others the fruit, whilst in others again it is certain excrescences produced by insects.

The production of leather is not, however, the only use to which these principles have been applied, for they give colorations with certain metallic oxides, and have, consequently, long been among the most valuable dyestuffs, being employed chiefly for the production of blacks, greys, and browns.

Tannin matters, or the commercial articles used for dyeing, being the bark, leaves, &c., of plants, invariably contain, besides the tannins peculiar to them, a certain amount of extraneous matter, such as gum, and woody fibre.

The tannins, or those principles which are the true dyestuffs, may be divided broadly into two classes, those which give a blue-black precipitate with persalts of iron, such as gall-nuts, Chinese galls, oak bark, sumach, dividivi, myrobalans, and valonia; and those which give a green coloration with persalts of iron, such as catechu, gambier, gum-kino, and elder, larch, and willow barks. Stenhouse has shown that most of the natural tannins which give a blue precipitate with persalts of iron are glucosides, whilst those which give a green one are not glucosides, with the exception, perhaps, of the tannin of willow bark.

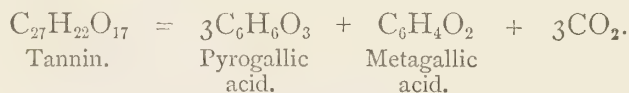
All the tannins are remarkable for the avidity with which they absorb oxygen in presence of the alkalis, becoming converted into bodies of various colours, green, red, brown, and black.

TANNIC, OR GALLOTANNIC ACID.—This, the most important of the tannins, which gives a blue-black with ferric salts, was first obtained by Prout in 1795. The best method of preparing it in a pure state, however, is that devised by Pelouze, who treated coarsely ground gall-nuts, in a displacement apparatus, with ether, which had been previously saturated with water, by being well shaken up with it. The ethereal solution which percolates through the gall-nuts separates into two layers, of which the upper one is ether, containing colouring matter, gallic acid, and other impurities; whilst the lower is a syrupy, aqueous solution of nearly pure tannin. This only requires to be carefully evaporated *in vacuo*, or at a low temperature, in order to obtain the tannic acid as a pale yellow, amorphous, spongy mass, inodorous, and having a most astringent taste. By this process one hundred parts



of good gall-nuts yield about sixty parts of tannin. Instead of aqueous ether, a mixture of dry ether with 5 per cent. of alcohol is very frequently used.

Tannin, as prepared by those methods, is almost insoluble in ether, but readily soluble in alcohol, and in water. It is precipitated from its aqueous solution by many of the stronger acids, and also by various salts, such as common salt, salammoniack, and potassium acetate. When boiled with baryta water, it yields barium gallate and glucate. Baryta or lime water in excess quickly colours tannin green, then blue, red, and finally a yellowish-brown. It gives a white precipitate with tartar emetic, or salts of lead; a characteristic blue-black one with persalts of iron, but none with the protosalts. It also gives precipitates with gelatin, and with the vegetable alkaloids. When treated with chromic acid, tannic acid is decomposed with evolution of carbonic anhydride; whilst with bichromate of potash it gives a yellowish-brown precipitate, which quickly turns black. It begins to decompose at about 400° F., carbonic anhydride being given off, whilst pyrogallic acid sublimes, and a black compound, called metagallic acid, remains in the retort. According to Strecker, the decomposition takes place in the following manner:—



As tannin obtained by the methods above described yields gallic acid and glucose when boiled with dilute acids, it was for a long time considered to be a glucoside of gallic acid, notwithstanding that the amount of glucose present in different specimens of tannin varied greatly. The recent researches of Schiff,\* however, have thrown much light on the subject, for by heating crystallised gallic acid with phosphorus oxychloride for several hours, he succeeded in

---

\* Ann. Chem. Pharm., clxx., 43, and clxxv., 165.

obtaining a substance possessing all the physical and chemical properties of ordinary tannin, but differing from it in being *perfectly free from glucose*. When boiled with dilute acids it is entirely converted into pure gallic acid, which may again be reconverted into tannin. From an examination of the acetyl derivatives of tannin, he came to the conclusion that it is an etherated anhydride of digallic acid, having the formula  $C_{14}H_{10}O_9$ , which is that originally assigned to it by Mulder. In a similar manner gallic acid is almost entirely converted into tannin by heating its concentrated aqueous solution with arsenic acid.

Although glucose is almost invariably present in natural tannin, yet it does not appear to be in the free state, that is, it is not a mere mechanical mixture of pure tannin and glucose. Schiff proposes to distinguish the natural product, containing glucose, as tannin; whilst the pure substance, free from glucose, may be called digallic acid.

In presence of alkalis, tannin absorbs oxygen from the atmosphere, and is converted into a red substance called *tannoxylic* or *rufitannic acid*. This acid, which has the formula  $C_7H_6O_6$ , may be prepared as follows:—a moderately strong solution of potash is saturated in the cold with tannic acid, and the solution, which soon turns red, is left to stand for some days until it becomes dark red and nearly opaque. It is then precipitated with acetate of lead; the resulting brick-red precipitate is treated with hot acetic acid, to dissolve undecomposed tannate of lead, and the tannoxylate of lead, which remains as a red precipitate, is decomposed by heating with alcohol and sulphuric acid. A dark red solution of tannoxylic acid is thereby obtained, which on evaporation leaves the acid as a brown-red amorphous substance.

GALLIC ACID.—This acid, which was discovered by Scheele, exists ready formed in several of the tannin matters, such as gall-nuts, sumach, valonia, dividivi, tea, &c.,



but is usually prepared by the transformation of the gallo-tannic acid of gall-nuts; for this purpose two processes are generally employed.

The first consists in reducing gall-nuts to a coarse powder, mixing it with water, and allowing it to stand for some weeks in a dark place, the temperature being maintained at from  $70^{\circ}$  to  $80^{\circ}$  F. A green mould forms on the surface soon after the fermentation sets in, and when it is complete the tannic acid will be found to be converted into gallic acid, mixed, however, with a small quantity of ellagic acid.

The second process, which is much more rapid, is based on the fact that the action of the stronger acids on tannin converts it into gallic acid. A strong decoction of gall-nuts is treated with strong sulphuric acid, when a pasty mass is thrown down, which is collected, washed with dilute acid, and pressed. It is then boiled for a few minutes with seven or eight times its weight of dilute sulphuric acid (one part of acid to ten of water), and allowed to cool, when impure gallic acid crystallises out. It may be purified by recrystallisation, or still better, by conversion into gallate of lead, which is washed, and decomposed by sulphuretted hydrogen. The sulphide of lead which is formed carries down and retains the colouring matters, whilst pure gallic acid remains in solution, and may be obtained on evaporation.

Gallic acid,  $C_7H_6O_5$ , forms white silky needles, which are sparingly soluble in cold water, but freely soluble in boiling water, alcohol, and ether. It has no odour, but an astringent, slightly acid taste. It gives no precipitate with proto-salts of iron, but a deep purple-blue with ferric salts. The author observed some years ago, that if this precipitate were kept for a few days it would be redissolved, the gallic acid reducing the peroxide of iron to the state of protoxide. Unlike tannin, it gives no precipitate with gelatin or albumen, which is a most important fact, as will be seen



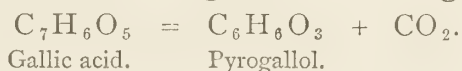
when we consider the application of tannin matters to dyeing and the preparation of leather.

With lime and baryta water, gallic acid gives a characteristic precipitate, white at first, but soon becoming green on contact with the air, and finally brownish-red. This affinity of the acid for oxygen in the presence of alkalis is far more active than that of tannin, as was shown by Chevreul in 1820, in his researches on the oxidation of colouring matters under the influence of alkalis. He suggested that tannin, or gallic acid might be used with advantage for the determination of the quantity of oxygen in gaseous mixtures. In 1838, Liebig again called attention to this property of gallic acid, and proposed the use of it, or still better, pyrogallic acid in gas analysis. The process, however, is not perfectly accurate, for in 1863, the author showed that a small portion of the oxygen is converted into carbonic oxide, the volume of that gas amounting to 3 or 4 per cent. of that of the oxygen absorbed when the gas operated on was pure oxygen, and about  $2\frac{1}{2}$  per cent. with air.

Gallic acid reduces the salts of gold and silver to the metallic state. It is a tribasic acid which expels carbonic acid from its salts, and forms three series of salts, containing one, two, and three equivalents of the base. Permanganate of potash decomposes gallic acid, oxidising it to carbonic acid and water. A volumetric method for the determination of gallic acid has been based on this reaction by Morin.

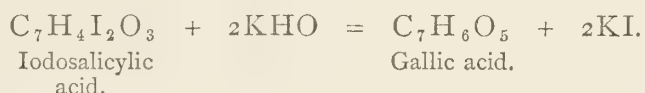
When gallic acid, or pure digallic acid, is heated with concentrated sulphuric acid, it loses the elements of water, and becomes converted into a red-coloured compound, *rufi-gallic acid*,  $C_{14}H_8O_8$ . On adding water to the mixture, the acid is thrown down as a red crystalline precipitate. It is only very slightly soluble in water, but it dissolves in alkaline solutions with a violet colour. It dyes mordanted cloth like alizarin, but the colours are dull.

When submitted to a temperature of  $212^{\circ}$  F., gallic acid loses two equivalents of water, and on being heated to about  $410^{\circ}$  F., it splits up into carbonic anhydride, and a beautiful white crystalline compound, called pyrogallic acid or pyrogallol, according to the following equation:—



At a higher temperature metagallic acid is also formed.

Gallic acid has been produced synthetically by treating di-iodosalicylic acid with a hot concentrated solution of potassium hydrate, the reaction being as follows:—



**PYROGALLIC ACID OR PYROGALLOL.**—This compound has acquired considerable importance of late years from the extensive use which has been made of it as a reducing agent in photography, and also from its application to reduce the metallic salts used with hair dyes. It was first observed by Scheele as a white sublimate, obtained on heating gallic acid. He, however, considered it to be sublimed gallic acid, and it is to Berzelius and Pelouze that we are indebted for establishing its composition.

The following process for obtaining pyrogallic acid commercially, was published by Stenhouse in 1843. Powdered gall-nuts are exhausted with water and the solution evaporated to dryness: the extract thus obtained, is reduced to powder and placed in a thin iron vessel having a flat bottom, on the top of which a perforated sheet of blotting paper is pasted, and over this a cardboard cone. A gentle heat is then applied, and gradually increased, until white vapours begin to escape from the top of the cone. As soon as the vapours cease to be given off, the cone is removed, when the pyrogallic acid is found on the surface of the blotting paper, and lining the interior of the cone. If the operation is carefully conducted the

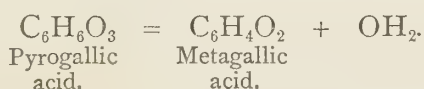
gall-nuts yield about 10 per cent. of the acid. Liebig has also proposed a good process, which consists in heating a mixture of crystallised gallic acid and pumice-stone in a glass retort, a current of carbonic acid being passed through it during the operation. One hundred parts of gallic acid thus yield from thirty to thirty-three of pyrogallol.

Pyrogallol is very soluble in water and in alcohol, somewhat less so in ether. It imparts an indigo-blue coloration to the protosalts of iron, and a red coloration with the persalts, but no precipitate is formed. It reduces the salts of gold, silver, mercury, and platinum to a metallic state, which renders it so useful in photography; with lime water it gives a fine purple colour, which is very characteristic, but soon changes to a deep brown.

In a dry state it undergoes no alteration in the air, but in solution it is quickly changed, becoming brown. This oxidation takes place very rapidly in the presence of alkalis, so that it may be substituted with advantage for gallic acid in the analysis of gaseous mixtures. On the evaporation of an alkaline solution of this acid, a black gummy residue is left, containing carbonate and acetate of the alkali metal.

Nitric acid converts pyrogallol into oxalic acid, and as its aqueous solution is turned brown by a mere trace of nitrous acid, it may be used as a reagent for the purpose of detecting the presence of that body. Pyrogallol is completely oxidised by permanganate of potash, so that the amount of the compound present in a solution, may be ascertained by a standard solution of this salt.

It fuses at  $240^{\circ}$  F., and boils at  $410^{\circ}$  F. At  $480^{\circ}$  F. it blackens, gives off water, and leaves an abundant residue of metagallic acid :





GALLEÏN.—This is a red dye, discovered by Baeyer,\* which is very similar in its properties to hæmateïn. It is prepared by heating a mixture of pyrogallol with phthalic anhydride to 390° F. for several hours. As soon as the reaction is complete, which is known by the mixture becoming thick, it is allowed to cool, then dissolved in boiling alcohol, filtered, and the filtrate poured into a large quantity of water. The brown precipitate of nearly pure galleïn thus produced may readily be obtained in a crystalline state by dissolving it in hot dilute alcohol and allowing the solution to cool. The crystals are brown by transmitted, but blue by reflected light; when its solutions are allowed to evaporate spontaneously, the residue has a greenish-yellow metallic lustre. Galleïn,  $C_{20}H_{12}O_7$ , is almost insoluble in cold water, and but little soluble in hot water, yielding, however, a red solution. It dissolves readily in alcohol, and also in alkaline solutions, the latter having a splendid blue or violet colour.

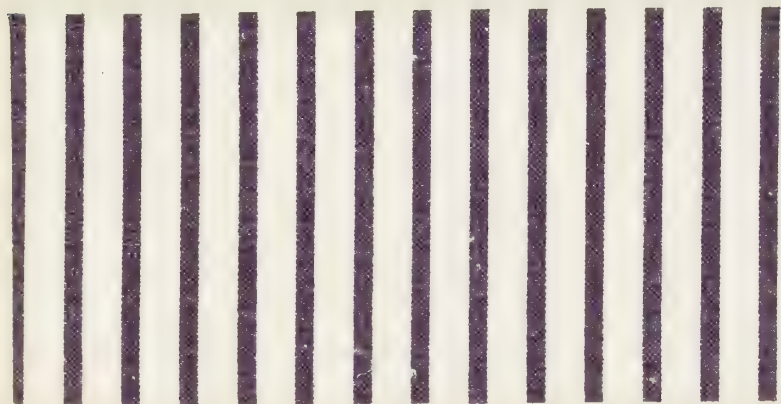
Galleïn, when treated with reducing agents such as zinc and sulphuric acid, is converted into a colourless compound, *gallin*,  $C_{20}H_{18}O_7$ , just as hæmateïn is converted into hæmatoxylin. The galleïn should be boiled with a large quantity of water and some sulphuric acid and zinc until the liquid becomes yellow. On cooling, oily drops separate, which soon solidify to a crystalline mass of impure gallin. It is best purified from the unaltered galleïn, by crystallisation from a hot solution of pyrogallol. It forms lustrous prisms, which are nearly colourless when first obtained, but gradually assume a red colour on exposure to the air, especially in the presence of ammoniacal vapours.

The colours which galleïn gives on cloth mordanted with alumina or iron have a bluer tinge than those obtained with logwood, and are finer and more stable, resembling those of barwood. With a lead mordant it produces a

---

\*Deut. Chem. Ges. Ber., iv., 457, 555, and 663.

brilliant violet-blue, which resists the action of soap extremely well. Similar colours are produced by gallin. The annexed interesting specimen, which we owe to the generosity of M. H. Koechlin, is galleïn, fixed by means of alumina and oxide of tin.



## GALLEÏN.

*Cæruleïn.*—This compound is formed when galleïn is heated with twenty times its weight of concentrated sulphuric acid to 390° F.; the red colour which the solution has at first, gradually changing to a greenish-brown. When the reaction is terminated,—which may be known by a sample giving dark flocks when heated with water, but without colouring the solution,—the product is poured into a large quantity of water, and the voluminous nearly black precipitate thoroughly washed with hot water. The precipitate, which consists of pure cæruleïn, has a composition represented by the formula  $C_{20}H_{10}O_7$ , and its formation from galleïn may be thus represented:—

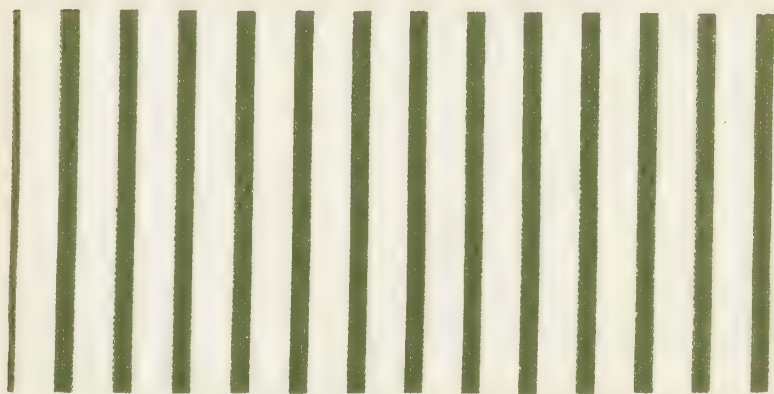


When dry it forms a bluish-black mass, which is but very slightly soluble in water, alcohol, or ether; it dissolves

readily, however, in hot aniline, with a magnificent blue colour, and this solution, when diluted with alcohol, and slightly acidified with acetic acid, dyes wool indigo-blue. Cœruleïn dissolves in alkaline solutions with a magnificent green colour, which is unaltered by exposure to the air, and yields green lakes with the earths. Cotton mordanted with alumina is dyed a fine green in a bath of this colour, whilst with iron mordants a brown is obtained. These shades resist soaping extremely well, and rival the madder colours in fastness.

Cœruleïn, when treated with reducing agents, behaves like galleïn, yielding a colourless substance, *cœrulïn*, which dissolves in ether, forming a yellow liquid with a beautiful green fluorescence. It is most easily obtained by acting on an ammoniacal solution of cœruleïn with zinc dust.

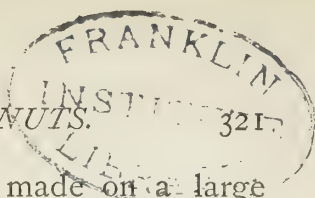
Cœruleïn resembles lo-kao in yielding a green alumina lake, and in being reduced by treatment with ammonia and zinc dust, although the difference in properties of the reduced products renders it extremely improbable that the two colouring matters are identical. The accompanying specimen of cœruleïn, which has also been presented by M. Koechlin, is fixed by means of alumina.



CÆRULEÏN.



ELLAGIC ACID.—GALL-NUTS.



Both galleïn and cœruleïn are now made on a large scale by Messrs. Durant and Huguenin, of Bâle.

ELLAGIC ACID.—This acid was discovered by Chevreul in 1815, who assigned to it the formula  $C_{14}H_6O_8, 2OH_2$ . Schiff finds, however, that the pure acid dried at  $230^{\circ}$  F. is  $C_{14}H_8O_9$ . It is deposited as a grey powder when a solution of gall-nuts is exposed to the atmosphere. To obtain it pure, the powder is thoroughly washed with water to remove the gallic acid, &c., then dissolved in potash, and precipitated from this solution by an acid. It is finally washed and dried. It has also been found amongst the products obtained by heating gallic acid with dry arsenic acid.

This acid is sometimes called *bezoardic acid*, from being found in certain oriental bezoars: these are intestinal calculi of various species of herbivorous animals, which eat the leaves of some astringent plants.

Ellagic acid is a light, pale yellow, crystalline powder, composed of very small transparent prisms which are insoluble in water, but soluble in alcohol. It colours a neutral solution of perchloride of iron, first greenish, but after a time, bluish black. This acid is soluble without decomposition in sulphuric acid, whilst nitric acid converts it into oxalic acid. Heated at  $212^{\circ}$  F. it loses a molecule of water, and at a higher temperature it is decomposed without previously entering into fusion, and leaves a charred mass covered with crystals.

GALL-NUTS.—These are the most valuable of all tannin matters. They are produced by the females of an insect called the *Cynips folii quercus*, which pierce the buds on the young branches of the *Quercus infectoria*, a tree growing especially in the East. The egg being deposited in the bud, the latter loses its natural growth and swells out to the size of a hazel nut, having a green, red, or pink colour. The eggs thus enclosed soon hatch, and the insect under-

goes all its metamorphoses until it attains the perfect state, when, if allowed (which is not to the interest of either the gatherer or consumer), it makes a hole and escapes. Good gall-nuts should not be so pierced, and they should be of a fresh bluish-green colour, having a prickly surface. If the insect has escaped, they are yellow, and are not of nearly so good quality, a great part of the tannic acid having disappeared. In the market, the nut-galls generally bear the name of the port from which they are shipped. Thus, there are Aleppo galls, which are considered the best, then the Morea, Smyrna, &c.

They have received many applications in various manufactures. The best qualities are employed in the preparation of tannic, gallic, and pyrogallic acids, and in the dyeing of silk. The white gall-nuts are used to produce blacks on morocco and other similar classes of leather.

The following may be considered as the composition of an average sample of gall-nuts:—

|                                   |       |
|-----------------------------------|-------|
| Tannic acid .....                 | 65.0  |
| Gallic acid.....                  | 2.0   |
| Ellagic acid .....                | 2.0   |
| Chlorophyll and Volatile oil..... | .7    |
| Brown extractive matter .....     | 2.5   |
| Gum .....                         | 2.5   |
| Starch .....                      | 2.0   |
| Lignin .....                      | 10.5  |
| Sugar albumen, &c., and ash ..... | 1.3   |
| Water.....                        | 11.5  |
|                                   | <hr/> |
|                                   | 100.0 |
|                                   | <hr/> |

A solution of gall-nuts gives the following reactions:—

|                                      |                     |
|--------------------------------------|---------------------|
| Salts of copper, chromium, and gold. | Brown precipitate.  |
| „ bismuth and mercury.               | Orange precipitate. |
| „ lead and antimony.                 | White precipitate.  |

|  |                                 |
|--|---------------------------------|
| Salts of silver, tin, cobalt, and cerium | { Dirty yellow precipitate.     |
| „ titanium.                              | { Blood-red precipitate.        |
| „ uranium.                               | { Red or chocolate precipitate. |
| „ platinum.                              | { Dark green precipitate.       |
| „ osmium.                                | { Bluish-purple precipitate.    |

Gall-nuts only impart a yellowish-green shade to animal fibres, but with an iron mordant they give shades varying from grey to bluish-black, according to the amount of mordant employed. They are used as mordants for various colouring matters in conjunction with alumina, and the order in which these two mordants are applied, makes a considerable difference in the intensity of shade obtained. If the alumina be first applied, and the fabrics then passed through a bath of decoction of galls, far more colour can be fixed than when the process is reversed.

Gall-nuts are the only available source for the production of tannic acid and its derivatives.

An inferior quality of gall-nuts is also sold, which is found on the *Quercus rubur*, an oak indigenous to Hungary, Styria, Croatia, and Piedmont, in which countries it grows with great luxuriance. It is a peculiar excrescence which prevents the growth of the acorn or gland, and in which the insect undergoes its metamorphosis. These gall-nuts bear the name of '*knopperns*', and are employed to tan leather, which they do more rapidly than oak bark. They are also used in Germany, in calico printing, to produce drabs, greys, and blacks.

CHINESE GALLS or JAPANESE GALLS.—These are about the size of a walnut, and very irregular in shape, having pointed and curved excrescences. They are formed upon



the leafstalks and branches of a species of sumach, *Rhus semialata*, which is common in Northern India, China, and Japan. They are remarkably rich in tannin, which appears to be of the same nature as that existing in ordinary Aleppo galls, since it furnishes gallic acid and pyrogallol when decomposed.

VALONIA.—*Valonia* is the commercial name for the large capsules or acorn cups of the *Quercus ægylops*, which are shipped in considerable quantities from Smyrna to Trieste and this country, where they are used for tanning, being much richer than bark in tannin matters. Valonia is sometimes employed to adulterate garancin, to which it imparts a greater power of dyeing purple shades.

SUMACH.—*Sumach*, as Stenhouse's researches have shown, is the only tanning or astringent matter, besides Chinese galls, in which the tannin is identical with that of gall-nuts. In sumach, however, there is a comparatively large quantity of gallic acid present, as also a soluble yellow principle.

Sumach is found in commerce as a coarse powder, obtained by grinding under mill-stones the leaves of several varieties of *Terebinthaceæ*. The species most cultivated is the *Rhus coriaria*, which came originally from Asia, but is now extensively grown in Sicily, France, Spain, and Portugal. The shrub attains a height of about 16 feet in the most arid soils, and the branches are cut down every year level with the ground.

There is a great difference in the amount of tannin matter found in the various sumachs which occur in commerce, but there is no doubt that that obtained from the *Rhus coriaria* is the best, whilst the most inferior is that grown in the south of France, the produce of the *Coriaria myrtifolia*. The sumachs imported into England bear the name of the countries whence they are obtained.

A decoction of sumach, which has a greenish-yellow

hue, and a peculiar odour, has a distinctly acid reaction, becomes turbid on cooling, and gives the following reactions:—

|                                    |  |
|------------------------------------|--|
| Gelatin.                           | Abundant white precipitate.  |
| Alkalis.                           | { White precipitate, which takes a green or reddish shade if an excess of alkali be added.                                 |
| Lime, baryta, and strontia waters. | { White precipitate, passing to green or red, on exposure to air.  |
| Acids.                             | Render it more or less turbid.   |
| Alum.                              | Abundant pale yellow precipitate.  |
| Acetate of lead.                   | { Flocculent canary-coloured precipitate.  |
| Acetate of copper.                 | { Flocculent yellowish-brown precipitate.  |
| Persulphate of iron.               | { Colours the liquor blue with a slight greenish tint, and gives an abundant blue precipitate.                             |
| Protochloride of tin.              | { Abundant yellowish-white precipitate.  |
| Tincture of iodine.                | { Produces a remarkable effect, developing a pink colour, which is soon destroyed.   |
| Chlorine.                          | { Appears to act in a similar manner, but the pink colour is weaker, and still more fugitive than that produced by iodine. |

In consequence of the powdered state in which sumach is sold, the tannin matter it contains is easily affected by contact with the air, and especially by damp, the gallotannic acid which it contains being gradually decomposed into gallic acid and glucose. Gallotannic acid combines with gelatin, albumen, or the animal matters existing in skins, producing an insoluble compound which fills the pores of the animal tissue, and thus contributes, not only to prevent

its putrefaction, but also to render it impermeable to water; gallic acid, however, does not combine with the animal matters, and can therefore take no part in the tanning or curing of a hide. It will thus be readily seen that exposure to the air or damp, rapidly deteriorates sumach for the purposes of the currier, but even if kept dry the same change goes on slowly, in consequence of the presence of a ferment, so that the longer a sample is kept the less value it has.

As already stated, gallic acid reduces the ferric salts (peroxide of iron) to the ferrous state (protoxide), the colour at the same time disappearing, so that it is not available for the purposes of the dyer of black silks, who uses sumach in conjunction with persalts of iron and gelatin for weighting the silk. For these purposes the tannic acid is the only valuable constituent of sumach, and it is of great importance to be able to ascertain with accuracy the amount of that substance present in any given sample. Although sumach is too expensive a tannin matter to be used for the tanning of common leather, yet it is employed by the currier in the preparation of skins for dyeing with light shades. It is also extensively used for the dyeing and weighting of black silk, although the colour so obtained is not equal to that of gall-nuts. Greys are also produced on silk by means of sumach.

Sumach, or more correctly the tannic acid it contains, is used as a mordant on cotton and flax fibres to fix colours which could not be otherwise employed; and this property of tannic acid is often enhanced by passing the goods, after they have been treated with sumach, through a bath of protochloride of tin. It is largely employed for this purpose in Yorkshire, either alone or in conjunction with salts of tin, to mordant the cotton warps of the mixed fabrics so extensively manufactured in that county. By this means the cotton takes the same colours as the woollen



weft, both with vegetable dyestuffs, and also with the aniline colours.

Sumach is used in the production of cheap garancin styles in calico printing, the tannin matters fixing the colouring matters of the dyewoods, and increasing the intensity of the purples and violets. An extract or decoction of sumach is also often used in printworks, to produce a bright yellow with salts of tin; and a dark yellow with sulphate of zinc. Sumach also, without a mordant, yields a yellow colour to wool and silk. From this we may infer that it contains a yellow colouring matter; the compound, however, has not as yet been isolated and studied.

A decoction of sumach must be used immediately it is made, as it contains a ferment called pectase, which at ordinary temperatures quickly decomposes the gallo tannic acid, whilst at 150° F. the fermentation takes place still more rapidly. For the same reason the extract rapidly deteriorates, becoming ropy, whilst at the same time an abundant brownish-yellow precipitate is produced. The author found some years ago that the addition of 1 per cent. of carbolic acid to a decoction of sumach prevented this decomposition taking place for a long time, and, as phenol is a neutral substance, it does not interfere in the least with the decoction, nor does it exert any injurious action on the colouring matters with which it comes in contact.

BABLAH.—*Bablah*,\* *Babool*, or *Neb-neb* is the fruit of several species of acacia. The principal varieties are East Indian bablah, from the *Acacia bambolah*; and Senegal and Egypt bablah, from *Acacia nilotica*. The pericarp of these fruits contains a dark brown astringent juice. The aqueous extract contains, according to Chevreul, gallic and tannic acids, red colouring matter, and a nitrogenous sub-

---

\* Watts' Dictionary of Chemistry, i., 480.

stance, besides other substances not yet examined. East Indian bablah yields to boiling water 49 per cent. of soluble matter; Senegal bablah 57 per cent.; nevertheless, according to Guibourt, the East Indian variety is richer in tannic and gallic acids, and therefore more valuable. Bablah is used in calico printing, in combination with iron and alumina mordants, to produce various shades of fawn colour. The tint produced by the seeds is different to that obtained with the husks; the seeds are said to contain a red colouring matter, and to be used in Egypt and India for dyeing morocco.

CHESNUT BARK.—An extract from the bark of the chesnut has long been used in Italy and the south of France, and is still largely employed in Lyons to produce cheap, fine, and fast blacks on silks. The solid extract has been introduced into this country for dyeing silks and cottons black.

DIVIDIVI.—*Dividivi* is the fruit of the *Cæsalpinia coriaria*. The plant is a native of the tropical part of South America. As imported into this country, it has the form of dark brown rolls containing a few flat seeds. It contains a large quantity of tannic acid, together with ready formed gallic acid.

MYROBALANS.—*Myrobalans*, are the dried nuts of the *Terminalia chebula*. It is imported chiefly from Calcutta, and is largely used for tanning leather, and producing blacks on wools.

OAK BARK.—*Oak bark* contains a glucoside called *quercitannic* acid, the composition of which has not yet been determined. It gives the same reactions with persalts of iron as gallo-tannic acid, but is not convertible into gallic acid, and does not yield pyrogallic acid on distillation.

SPRUCE BARK, or HEMLOCK TREE.—Mr. J. L. Norton, has proposed to use the extract of the bark of the hemlock spruce, or *Abies canadensis*, as a substitute for that of

sumach in fixing the colouring matters obtained from coal-tar. It is used for quick tanning.

WALNUT HUSKS.—A preparation from the husk of the walnut, called *Brou-de-noix*, has long been employed, and is still frequently used at the Gobelins, to obtain reddish-brown hues, which are very fast, and do not require any mordants. It is also employed to impart a darker shade to certain colours. It is prepared by putting very ripe walnuts into a cask with water, when after some time it is ready for use as a dyestuff.

Mr. Phipson\* has obtained from the husks of walnuts, a yellow substance, crystallising in octahedra, to which he has given the name *regianin*. It rapidly oxidises to a black acid, which he calls *regianic acid*. He has also separated a body similar to tannin, to which he gives the name of *nucitannin*. Under the influence of mineral acids it splits up into glucose, ellagic acid, and a new compound, *rhotic acid*.

HENNIS.—Before passing from this class of tannin substances, there is one which ought to be noticed, as it has been used from the most ancient times in Egypt, Arabia, and other Eastern countries, to dye wool, horse-hair, leather, &c. It is made from the leaves of the *Lawsonia inermis*, which appears to be the *gopherwood* of Scripture, and the *hennis* of the Egyptians. The leaves are mixed with water to form a paste of an orange-brown colour. This paste is also employed by the Asiatic ladies to dye the nails of their hands and feet, as well as their ears and hair.

CATECHU, CUTCH, OR TERRA-JAPONICA, GAMBIE, AND KINO.—*Catechu* and *gambier* are the most valuable of the tannin substances which give a green coloration with persalts of iron. They are very extensively used to produce a great number of shades, varying from light drabs to dark

---

\*Compt. Rend, lxxix, 1372.



brown, in cheap, dyed cotton goods, such as fustians and corduroys. They are used in calico printing chiefly to produce browns, in silk dyeing to weight the silk, and in tanning to produce a low class of leather, easily distinguishable from that tanned with bark and other matters belonging to the first class, because when used for making shoes it communicates to the stockings a peculiar orange-yellow hue.

For a long time there was much doubt as to the genus of plants from which catechu, gambier, and kino, which resemble each other very closely in their properties, were derived. M. Guibourt, a few years ago solved the problem. He found that real *catechu*, *cutch*, or *terra-japonica*, which has been used in the East both in medicine, dyeing, and tanning from time immemorial, is derived partly from the softer parts of the wood and the pods of the *Acacia catechu*, a tree belonging to the leguminous order, and partly from the betel or areca nut, the fruit of the areca palm, or the *Areca catechu*. These nuts, which are about the size of a nutmeg and have somewhat the same appearance, are largely used as a masticatory in Eastern countries. For this purpose the crushed nut is generally used along with the leaf of the betel pepper, and chunam or shell-lime. To prepare catechu, the wood or nuts are boiled in water, and when the solution has been evaporated to the consistence of a syrup, it is spread on leaves or on the ground, and solidifies on cooling.

*Gambier* is extracted from the leaves of the *Uncaria gambir*, a shrub very abundant in India and the Malacca Islands. The shrub belongs to the family *Rubiaceæ* and to the same tribe as the *cinchona*.

*Kino*, improperly named in commerce *gum-kino*, is furnished by several Indian plants, especially by the *Butea frondosa*, belonging to the *Leguminosæ* and the *Pterocarpus marsupium*. It is used in India as a dyestuff for cottons, and

also as a medicine, but as it is not employed by English dyers it is unnecessary to enter into a minute description of it.

There are several varieties of catechu in commerce, but the three which are principally used by dyers and calico printers are all that need be noticed. The *Bombay catechu*, which is the best, is obtained from the *Areca catechu*, and occurs in dense, irregular lumps, of a dark brown colour, weighing from 80 to 90 lbs., and is covered with leaves. It is opaque, with an even, slightly unctuous, shining fracture. Bombay catechu is almost entirely soluble in boiling water, yields a dark brown liquor very rich in tannic acid, and affords copious precipitates with gelatin, and with sulphuric acid.

*Bengal catechu* is obtained from the *Acacia catechu*. It has a lower specific gravity than the Bombay variety, and is of a pale brown colour, with a yellowish cast. It is opaque, with a glimmering lustre on the fractured surface only, and is traversed by dark brown shining stripes. When treated with cold water it leaves a large residuum, but it is almost entirely dissolved by boiling water; the solution contains less tannin, but more catechin, than that from the Bombay variety.

*Gambier catechu* is imported from Batavia, and occurs in cubical pieces of about an inch or rather more in size: it is opaque, and of a brownish-yellow or bright yellow colour. Its fracture is even and dull. It is only slightly soluble in cold water, but almost completely in boiling water, the solution affording copious precipitates with gelatin, and with sulphuric acid.

All these products have an astringent taste, with a sweet after flavour. They are soluble in alcohol, acetic acid, and the alkalis, to which they impart a reddish-brown colour.

The aqueous solution yields the following reactions:—

|                       |  |
|-----------------------|--|
| Gelatin.              | Abundant reddish-white precipitate.            |
| Alkalis.              | Give it a decidedly brownish hue.              |
| Lime water.           | Yellowish coloration and precipitate.          |
| Salts of alumina.     | { Clear the liquor, giving it a yellowish hue. |
| Protosalts of iron.   | Olive-green coloration.                        |
| Persulphate of iron.  | Dark green coloration.                         |
| Sulphate of copper.   | Olive coloration.                              |
| Acetate of copper.    | { Abundant blackish-brown precipitate.         |
| Salts of lead.        | Yellowish-grey precipitate.                    |
| Bichromate of potash. | Abundant brown precipitate.                    |

Stenhouse was unable to obtain any glucoside by the action of boiling dilute acid on catechu. Catechu, besides varying widely in quality, is freely adulterated with mineral substances, starch, tannin matters, and blood. Good catechu should not contain more than 4 to 5 per cent. of ash. To ascertain the presence of starch, the sample is first treated with alcohol, and the insoluble residue then boiled with water; if starch be present the solution will give a fine blue coloration on the addition of iodine. The presence of any ordinary tannin matter in the catechu will modify the green coloration, which the latter substance gives with the persalts of iron. Blood may be detected, if present, by treating the catechu with alcohol, and after drying the insoluble residue, heating it in a tube, when ammoniacal vapours will be given off, and a most offensive odour produced. Good catechu should not leave more than 12 per cent. of insoluble matter when treated with boiling alcohol.

Sometimes the yellow gambier is transformed into brown catechu by melting it and adding 1 per cent. of bichromate of potash, which imparts oxygen to the catechin, converting it into a brown resinous body. The melted mass is then poured into wooden frames, and when cold has a conchoidal fracture. This fraud may be easily discovered



by calcining the catechu, and testing the ash for oxide of chromium. The best method, however, of ascertaining the value of catechu, is to make comparative printing essays with the sample to be tested and one of known good quality. To effect this, Schützenberger recommends that 2 ozs. of catechu be mixed with 4 ozs. of vinegar, and thickened with gum. The mixture is then printed on the fabric, which is afterwards steamed and passed through a weak solution of bichromate of potash. After being washed and dried, the intensity of the colour produced by the different samples may be compared.

Catechu is composed of three substances, namely, a tannin matter soluble in cold water, which has received the name of cachoutannic, catechutannic, or mimotannic acid, a white crystalline body called catechin, or catechuic acid, and a brown amorphous matter formed by the oxidation of catechin, during the evaporation of the decoctions of the plant or nuts.

*Catechutannic acid.*—The best method of preparing this acid is that of Loewe,\* who boils the pulverised catechu with water, and after allowing it to stand for some days, separates the catechin which has crystallised out, by filtration. The aqueous solution of the impure acid is carefully evaporated to dryness, dissolved in alcohol and filtered, sulphuric acid being added to precipitate any lime that may be present. In order to remove the excess of sulphuric acid, lead carbonate is added, and the lead in solution subsequently precipitated by sulphuretted hydrogen: ether is then added, to precipitate various resinous matters, and the solution evaporated. After the residue has been dissolved in water, and agitated with ether, to remove a small quantity of catechin which is present, a solution is obtained which, on evaporation, leaves pure catechutannic acid. Pelouze, assigns to this acid the formula  $C_{18}H_{18}O_8$ , but Loewe, who

---

\*Jour. für pr. Chem., cv., 32, 75.

has more recently examined the subject, makes it  $C_{15}H_{14}O_6$ . Davy and Nees found that Bombay catechu, contained about 54.4 per cent. of the acid, that from Bengal 48.2, and Gambir 36 to 40.

It is readily soluble in water and alcohol, but insoluble in ether. Its aqueous solution gives precipitates with gelatin and with tartar emetic, and a green precipitate with the persalts of iron.

On exposure to the atmosphere an aqueous solution of this acid is gradually oxidised, becoming of a reddish colour; when alkalis are present this change takes place much more rapidly.

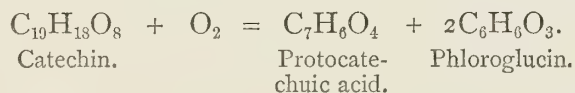
*Catechin*, or *catechuic acid*, may readily be obtained from the impure catechin obtained in the preparation of catechutannic acid, or from the residue left on exhausting powdered catechin with cold water. This is dissolved in about eight parts of boiling water containing a little acetic acid, and lead acetate added. After separating the precipitate by filtration, a current of sulphuretted hydrogen is passed through the liquid to remove the lead in solution, and it is put aside to crystallise in a dark place. Or, the impure catechin may be crystallised several times from boiling water, with the addition of animal charcoal.\*

The true formula for catechin is at present very doubtful. Loewe makes anhydrous catechin  $C_{16}H_{14}O_5$ , Kraut and van Delden  $C_{12}H_{12}O_5$ , whilst Hlasiwetz and Malin, who find that catechin when fused with caustic potash is decom-

---

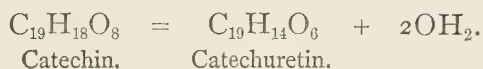
\* As catechutannic acid, contrary to the statements in most handbooks, is insoluble in dry ether, whilst anhydrous catechin is readily soluble, the latter may be advantageously prepared by exhausting finely powdered catechin, which has been dried at  $212^{\circ}$  F., with dry ether. On filtering the solution, and distilling off the ether on the water bath, a pale yellow, thick oily fluid is left, which, if poured out and exposed to the air for a few days, attracts moisture and becomes converted into a crystalline mass of pure catechin. If a pale-coloured catechu is selected, this forms by far the most convenient process for obtaining pure catechin, whilst the residue, insoluble in ether, readily affords catechutannic acid when treated by Loewe's process.—EDS.

posed into *protocatechuic acid* and phloroglucin, consider it to be  $C_{19}H_{18}O_8$ , and represent the decomposition just mentioned in the following manner:—



The amount of protocatechuic acid obtained by this means is very small however.

Catechin is a white, silky, crystalline substance, consisting of microscopic needles. It is very sparingly soluble in cold water, but freely soluble in boiling water, its solutions being neutral to litmus. It is also readily soluble in alcohol and in ether. An alkaline solution of catechin rapidly acquires a brown hue, and if acetic acid be now added to it, the colour becomes less intense, and it gives a precipitate with gelatin. When boiled with dilute sulphuric acid out of contact with air, it is decomposed with formation of a brown powder, which has received the name of *catechuretin*. The following equation represents the reaction which takes place:—



By dry distillation catechin yields pyrocatechin.

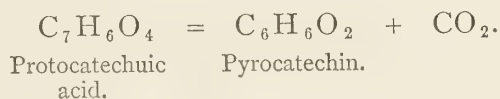
According to Svanberg, a solution of catechin, in presence of caustic alkalis, rapidly absorbs oxygen, being converted into *japonic acid*, which, on the addition of hydrochloric acid, is thrown down as a black precipitate. In presence of alkaline carbonates, catechin is converted into a red compound called *rubinic acid*; this compound is, however, very unstable.

Protocatechuic acid is produced not only from catechu, but also when piperic acid, gamboge, scöparin, dragon's blood, the tannin of the horse chesnut, or of larch bark, and many other vegetable substances are fused with potash; it is, however, most conveniently prepared from kino. In



order to extract it, the fused mass is dissolved in water, acidulated with sulphuric acid, and the filtered solution agitated with ether. On evaporating the ethereal solution, a crystalline mass is left, which may be purified by pressure between bibulous paper, and recrystallisation.

Protocatechuic acid forms thin prismatic needles, or laminæ, having the formula  $C_7H_6O_4, OH_2$ . It is soluble in water, alcohol, and ether. Its aqueous solution gives a dark blue coloration with perchloride of iron, which becomes red on the addition of an alkali. When heated to  $212^\circ F.$  it loses an equivalent of water, and the dehydrated acid then melts at  $390^\circ F.$  It is decomposed by dry distillation into pyrocatechin and carbonic anhydride.



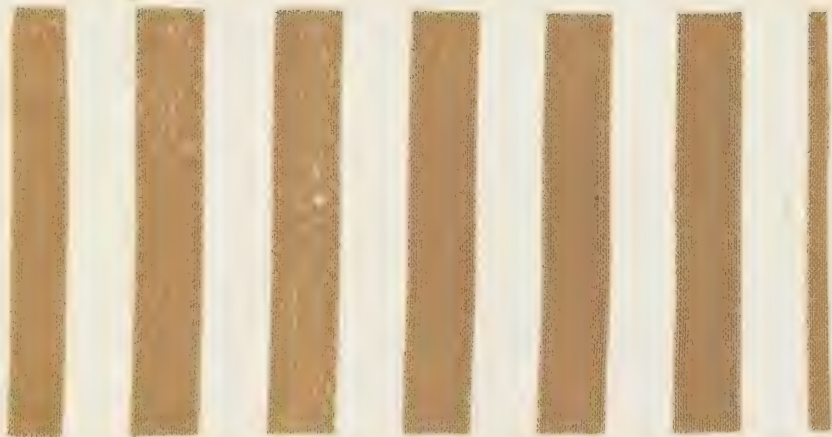
*Pyrocatechin* or *pyrocatechuic acid*, formerly called *oxyphenic acid*, besides being produced from catechin and protocatechuic acid, is obtained, according to Eissfeldt and Uloth, by the dry distillation of all those kinds of tannin which turn persalts of iron green. When pure, it forms thin white lustrous laminæ, resembling benzoic acid in appearance. It fuses at  $240^\circ F.$ , and dissolves readily in water and alcohol. It is also soluble in ether and in benzene. It gives with persalts of iron a dark green coloration, a black precipitate being deposited after a time; with gelatin it gives no precipitate.

Loewe considers that catechu contains, besides the catechin and catechutannic acid, three other substances soluble in water, namely—*mimotannihydroretin* and the japonic and rubinic acids already mentioned; they are soluble in alcohol, but precipitated from that solution by ether.

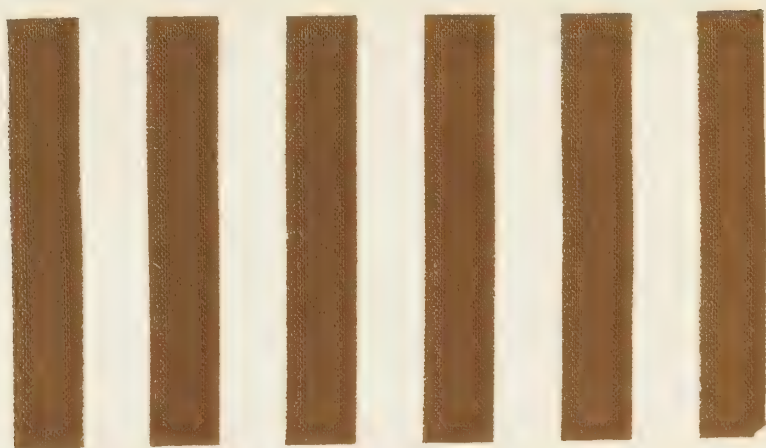
Catechu is extensively employed for dyeing cotton, especially fustians, owing to the great variety of drab

shades which it yields with various mordants. By these means, greenish or grey-drab shades are produced with aluminous mordants alone; yellow-drabs, light yellows, and chamois tints, with chloride of tin, to which red tints may also be imparted by means of the red dyewoods; and various shades of brown with iron mordants, which may be fixed and intensified by passing the goods through a weak bath of bichromate of potash.

Dyers avail themselves of the colouring properties of both catechutannic acid and catechin, whilst the calico printer, who uses the catechu merely for the production of browns, requires only the catechin, which he introduces into the fibre, and then oxidises into the insoluble japonic acid. The process employed is as follows:—A hot decoction of catechu is made, acetic acid or caustic soda being added, and the solution filtered through filtering cloth. If light shades are required, it is thickened and printed on the fabric, which is then exposed to the atmosphere for oxidation; if darker ones are required the fabric is passed through a weak solution of bichromate of potash; whilst if rich dark browns are to be produced, a salt of copper, and



CATECHU BROWN (LIGHT SHADE).



CATECHU BROWN (DARK SHADE).

salammoniac are added to the thickened decoction before printing, the goods being subsequently steamed and passed through a bichromate bath. The copper salts and bichromate of potash completely oxidise the catechin into japonic acid, giving thus the rich catechu browns so much used at present. The preceding light and dark brown samples we owe to the kindness of Messrs. Salis Schwabe and Co., of Manchester.

If dyers, instead of employing catechu as imported, were to grind it, and wash with cold water, they would obtain an extract which would yield very pure shades of green-drabs, whilst the insoluble residue of catechin would give a great variety of tints.

DETERMINATION OF TANNIN.—From the facts already stated, it must be obvious to all who use tannin matters, whether tanners or dyers, that these substances not only vary in value, according to the variety of plant from which they have been obtained, and the country whence they are imported, but by the wilful addition of foreign matters such as starch, ochre, &c., to catechus; sand, and other mineral substances to sumachs, these being sources of deterioration which cannot be detected by mere inspection.



There is again another class of adulterations, such as the addition to a new sumach of a quantity of a comparatively old one, a fraud which it is impossible to discover by the eye. The only method therefore of ascertaining the value of the various astringent substances met with in commerce, is to determine chemically the amount of tannin they contain. This may be done with great accuracy by the following process:—A weighed quantity (say 100 grains) of the substance to be tested is boiled with distilled water, and the decoction run off into a beaker without filtering. This process is repeated four or five times. A test solution is prepared by dissolving 1 drachm of gelatin in 4 ozs. of water, and adding 15 grains of powdered alum to the solution. One hundred and fifty-five grains of this solution represent about 5 grains of pure tannin. The test fluid is carefully dropped into the beaker until, on the falling of a drop upon the surface, the characteristic ring of tannate of gelatin is no longer produced. In most cases the supernatant liquid is not perfectly clear, so that it is difficult to ascertain when the exact amount of the gelatin solution has been added. In this case it is better to filter a small portion of the solution, which may be readily done by means of a glass tube, into the end of which a piece of good sponge has been inserted. This end of the tube is plunged into the liquid and suction applied. The quantity of test fluid used is then ascertained, and from this the percentage of tannin is calculated by comparison with the amount required to precipitate a solution containing a known quantity of pure tannin. The above process, when carefully carried out, will give correct results as to the comparative value of tannin matters.

Although several elegant and rapid processes, based on the employment of oxidising agents, have been proposed for determining the value of tannin substances, yet there are sources of serious error arising from the presence of

other oxidisable substances, such for instance as gallic acid, which are of no value whatever either to the dyer, the calico printer, or the tanner.

The following table, taken from Dr. Ure's work, shows the quantity of extractive matter and tannin in 100 parts of several substances:

|                                     | In 480<br>by<br>Davy. | In 8 oz.<br>by<br>Biggins. | In 100<br>parts by<br>Cadet de<br>Gassin-<br>court. |
|-------------------------------------|-----------------------|----------------------------|---|
| White inner bark of old oak .....   | 72                    | ...                        | 21  |
| „ young oak .....                   | 77                    | ...                        | ...   |
| „ Spanish chesnut ...               | 63                    | 30                         | ...   |
| „ Leicester willow...               | 79                    | ...                        | ...   |
| Coloured or middle bark of oak..... | 19                    | ...                        | ...   |
| „ Spanish                           |                       |                            |   |
| chesnut...                          | 14                    | ...                        | ...   |
| „ Leicester                         |                       |                            |   |
| willow ...                          | 16                    | ...                        | ...   |
| Entire bark of oak .....            | 29                    | ...                        | ...   |
| „ Spanish chesnut ...               | 21                    | ...                        | ...   |
| „ Leicester willow ...              | 33                    | 109                        | ...   |
| „ elm .....                         | 13                    | 28                         | ...   |
| common willow ...                   | 11                    | (boughs)                   | 31 ...  |
| Sicilian sumach .....               | 78                    | 158                        | ...   |
| Malaga sumach .....                 | 79                    | ...                        | ...   |
| Souchong tea .....                  | 48                    | ...                        | ...   |
| Green tea .....                     | 41                    | ...                        | ...   |
| Bombay catechu .....                | 261                   | ...                        | ...   |
| Bengal catechu.....                 | 231                   | ...                        | ...   |
| Gall-nuts .....                     | 127                   | ...                        | 46  |
| Bark of oak, cut in winter .....    | ...                   | 0                          | ...   |
| „ beech .....                       | ...                   | 31                         | ...   |
| „ elder .....                       | ...                   | 41                         | ...   |
| „ plum-tree.....                    | ...                   | 58                         | ...   |
| „ trunk of willow .....             | ...                   | 52                         | ...   |
| „ sycamore .....                    | ...                   | 53                         | 16  |

*SUBSTANCES YIELDING TANNIN.*

341

|                                    | In 480<br>by<br>Davy. | In 8 oz.<br>by<br>Biggins. | In 100<br>parts by<br>Cadet de<br>Gassin-<br>court. |
|------------------------------------|-----------------------|----------------------------|---|
| Bark of birch .....                | ...                   | 54                         | ...   |
| „ cherry-tree .....                | ...                   | 59                         | 24  |
| „ sallow .....                     | ...                   | 59                         | ...   |
| „ poplar .... ..                   | ...                   | 76                         | ...   |
| „ hazel .....                      | ...                   | 79                         | ...   |
| „ ash .....                        | ...                   | 82                         | ...   |
| „ trunk of Spanish chesnut .....   | ...                   | 98                         | ...   |
| „ smooth oak .....                 | ...                   | 104                        | ...   |
| „ oak cut in spring .....          | ...                   | 108                        | ...   |
| „ alder .....                      | ...                   | ...                        | 36  |
| „ apricot .....                    | ...                   | ...                        | 32  |
| „ pomegranate .....                | ...                   | ...                        | 32  |
| „ Cornish cherry-tree.....         | ...                   | ...                        | 19  |
| „ weeping willow .....             | ...                   | ...                        | 16  |
| „ Bohemian olive .....             | ...                   | ...                        | 14  |
| „ tan shrub, with myrtle leaves... | ...                   | ...                        | 13  |
| „ Virginian sumach .....           | ...                   | ...                        | 10  |
| „ green oak .....                  | ...                   | ...                        | 10  |
| „ service-tree .....               | ...                   | ...                        | 8   |
| „ rose chesnut of America .....    | ...                   | ...                        | 8   |
| „ rose chesnut .....               | ...                   | ...                        | 6   |
| „ rose chesnut of Carolina .....   | ...                   | ...                        | 6   |
| „ sumach of Carolina.....          | ...                   | ...                        | 5   |
| Root of tormentil.....             | ...                   | ...                        | 46  |
| Cornus sanguinea of Canada .....   | ...                   | ...                        | 44  |



## CHAPTER XI.

### ON THE EXAMINATION OF COLOURING MATTERS AND COLOURED FABRICS.

The previous chapters having been devoted to a consideration of the properties of the various colouring matters other than those derived from coal-tar, it will now be advisable to notice the methods employed for the determination of the nature of a colouring matter fixed on a fabric; to recapitulate to some extent the methods of detection of various adulterations; and to give the most important processes for determining the comparative commercial value of particular samples.

Beginning with the latter point as the least complex, we may premise that in many cases it is impossible, and in nearly all extremely tedious and difficult to separate the colouring matters in a state sufficiently pure, or in such a definite combination as to enable us to weigh them directly: we must therefore adopt the artifice of making a comparison of the sample, the value of which it is desired to ascertain, with that of a standard sample of known good quality, or having a known value.

In many cases the simplest method of doing this is by means of an instrument called the 'colorometer,' in which the depth of colour of solutions of the sample to be tested and of the standard may be compared. A known weight of the colouring matter is taken, and the colour extracted by water, or alcohol, or in some cases by a solution of alum, or some other solvent especially adapted to the colouring matter under consideration. The solutions, when made up to an equal volume, are ready for comparison.

The earliest instrument devised for this purpose was that of M. Houton-Labillardière. It is very simple, being composed of two glass tubes, about half-an-inch wide and 14 or 15 inches high, closed at the bottom, and placed side by side on a stand. The tubes are graduated either throughout their entire length or only on the upper half. A quantity of the solution to be tested is then placed in one of the tubes, filling it one-half. The standard solution is then filled to the same point in the other tube, and water, or alcohol, as the case may be, is added to the darker solution (which will in most cases be the standard,) until the depth of colour in both tubes is the same. The values of the two samples will of course be in direct proportion to the relative volumes of the solutions in the tubes when the intensity of the tint is the same in both. Thus, suppose fifty divisions of the original solution has been taken, and it has been necessary to add ten divisions of water to the standard, the value of the standard sample and that to be tested will be as  $60 : 50 :: 100 : 83.33$ , or the sample contains five-sixths of the colouring principle that the standard does. This apparatus may be replaced by two burettes of the same diameter.

The first improvement on this plan was to place the tubes in an oblong box, Fig. 12, a kind of camera obscura, having two holes in the top, near one end, of a diameter equal to that of the tubes. At the end, directly in a line with these holes, are two slits, also the same width as the tubes. At the other end is a hole by which, on placing the tubes containing the solutions

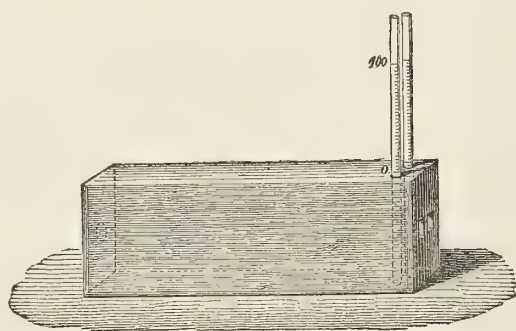


FIG. 12.

in the apparatus, and turning the slits to the light, the lower portion of the tubes can be seen. As no light falls on them, except through the slits, greater accuracy may be obtained than by the first method.

M. Collardeau has proposed an instrument on a somewhat different principle: instead of diluting the stronger liquid, he lengthens the column of the weaker fluid, until, on looking through it, the intensity of colour appears the same, and the values are in inverse ratio to the length of the columns. His apparatus consists of two tubes, T, T', Fig. 13, fixed horizontally on a support, and which can be drawn out like

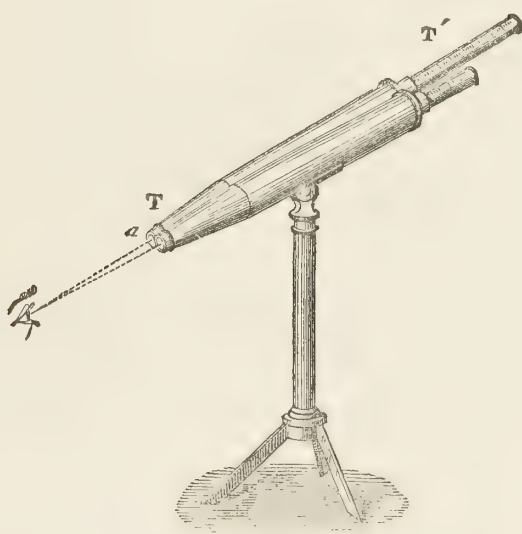


FIG. 13.

a telescope; they are impermeable, and are closed at their extremities *a*, by discs of glass. The sliding tubes are furnished with scales, by which the depth of column may be ascertained. By means of a small tube communicating with the vessels containing the respective liquids, the larger tube may be kept filled.

M. A. Müller has described an instrument depending for its action on the production of white light, by passing the light first through the coloured solution, and then through a disc of glass of the colour complementary to that of the solution. The difference of the depth of columns necessary to produce the white light giving the difference in value.

MM. Dubosc and Mene, have proposed an apparatus consisting of parallel tin tubes to contain the liquids. At



the lower part of the tubes a mirror is fixed similar to that for a microscope. At the upper part of the tubes prisms are so placed that the light from them forms, at the point of sight, a disc divided into two parts, consequently, when the liquids are equally coloured, there will be a uniform coloration of the disc. An instrument on this principle, devised by Mr. R. P. Wilson, is now employed in testing the value of petroleum, with the difference, however, that the colour of the standard is obtained by means of stained glass, but with a very little alteration this instrument would be well adapted for a colorometer. Fig. 14, represents Mr. Wilson's apparatus: *a, a, a*, is one of the two tubes which

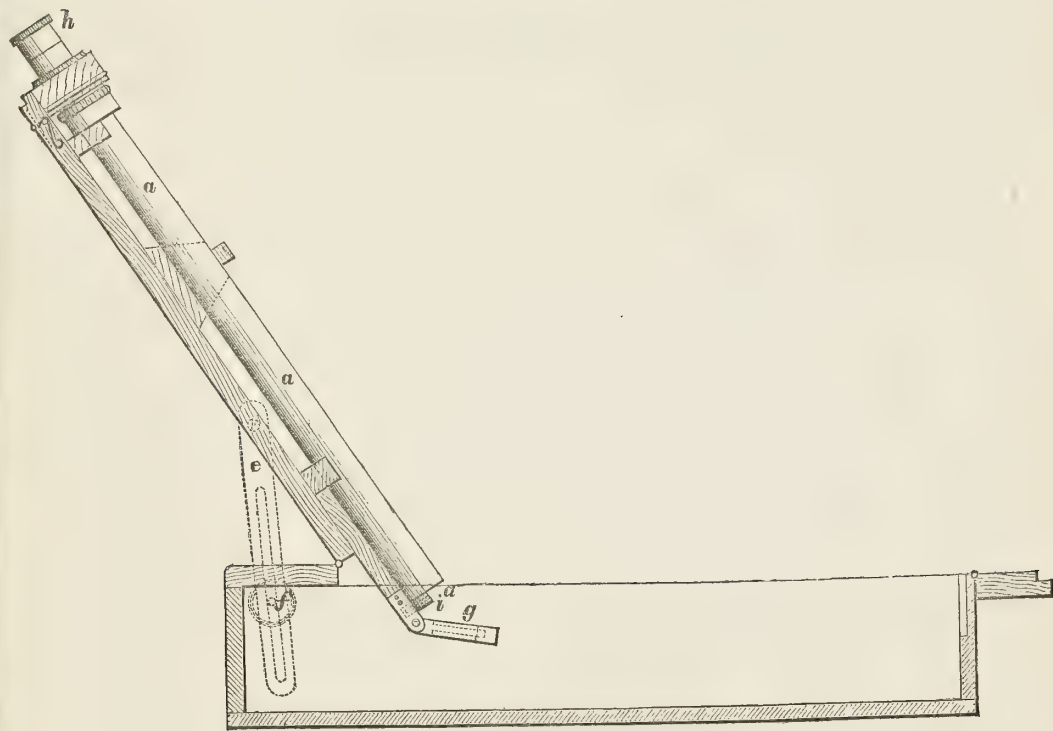


FIG. 14.

are attached side by side to the hinged lid of the box, and filled with the two liquids, the colours of which are to be compared; *g* is a mirror by which the light is reflected and caused to pass through the two tubes, where it is received

at the upper end on glass prisms. These are so arranged that on looking through the eye-piece *h*, a circular field is seen divided down the centre by a perpendicular line ; one half of the field being illuminated with the light which has passed through one tube, and the other half with the light which has passed through the second tube. By this means the colour of the two semi-circular discs may readily be compared. The piece marked *e, f*, is a link furnished with a set screw, so that the lid of the box to which the tubes are attached, may be set at any desired angle ; whilst at *i*, pieces of standard coloured glass may be introduced for comparison opposite the end of one of the tubes, which in that case is filled with water.

Closely allied to colorimetry is the detection of colours by means of the spectroscope, but this, of course, can only be a qualitative not a quantitative process. There is no doubt that before very long, this instrument will prove a most valuable addition to our means of ascertaining the presence of small quantities of colours. When speaking of madder we have already had occasion to refer to the marked difference observed by Professor Stokes, between the spectrum of alizarin, and that of purpurin. He also studied the spectrum of hæmatosin, the colouring matter of blood, and the results obtained by him were so remarkable that they attracted the attention of Mr. H. C. Sorby, who has devised an apparatus by means of which solutions of the colouring matters can be examined spectroscopically. This method has already been applied very successfully to the determination of the age of wines, and also to the detection of certain adulterations, but as the spectra of those colouring matters which are usually met with in commerce, are at present to a great extent unknown, the suggestions he has given for a general method of procedure in the examination of colouring matters, has not as yet been rendered practically available.

A second method of determining the relative value of two samples of colour is by means of oxidising agents; some processes of this nature, applicable in particular cases, have been already described, but it must be remembered that they are unreliable in direct proportion to the facility with which the oxidising agent employed is reduced by organic matters generally; whilst even in the most favourable instances, the results obtained ought to be confirmed by some other process. This is well illustrated in the case of indigo. If a sample of indigo, which will only yield to the dyer 60 per cent. of available colouring matter, be tested by the oxidation process, it will show from 70 to 80 per cent. of indigotin; other organic matters in the indigo being oxidised at the same time. The oxidising agents which have been proposed are permanganate of potash, bleaching powder, chromic acid, bichromate of potash, and potassium ferricyanide.

The third and most certain means of comparison is founded on the relative dyeing powers of the samples and the standard, and is, in fact, the carrying out on a small scale of the processes followed on the large scale in the dye-works. The apparatus best adapted for this purpose has been already described at the close of the third chapter (p. 105): the questions of temperature and time of course vary with each dyestuff, and will be found described under the respective colouring matters, or if not, may be gathered from their properties. In all cases, however, the experiments on the samples to be compared must be carried on at the same time, under exactly the same conditions; great care being taken not to have an excess of the colouring matter, for the object is not to produce beauty of shade in the dyed samples, but to ascertain the relative amounts of colour in the respective dyestuffs; this can only be effected by employing a smaller amount of colouring matter than is necessary to obtain a full tone.



The principal mineral adulterations to which dyestuffs are liable are sand and clay with red colouring matters; powdered brick with yellow colouring matters; ochre with tannin matters; chalk and white lead, and even an aluminous lake of logwood, with indigo; whilst talc and white lead are common adulterations of cochineal. These may all be easily detected by calcination, the amount of residue showing whether any fraudulent addition of mineral matter has been made. Starch is also an article commonly used for purposes of adulteration. The presence of this body may be proved by treating the dyestuff with dilute alcohol, and then with cold water, which will in most cases remove the colouring principle; on afterwards treating the residue with boiling water, the starch will be dissolved, and may be recognised by the blue coloration produced on adding a few drops of tincture of iodine. The addition of a wood or bark from which the colouring matter has been already extracted is also sometimes resorted to, and although in some cases it may not be possible to prove such addition, yet the low dyeing power of such a sample will always be shown in a comparative test, and its inferior value will be manifested. The special adulterations to which individual dyestuffs are liable having already been noticed when treating of them, it is unnecessary to enter into the details here.

The reactions offered by colours fixed on tissues are very varied, and are also subject to modification, according to the nature of the fibre on which they are fixed, but the tables taken from the work of the late Professor Bolley, which are given as an appendix at the end of the book, are sufficient to guide the analyst as to the nature of the colouring matter, and in most cases also as to the manner in which it has been applied. The nature of the mordant is ascertained by the incineration of a portion of the tissue and the examination of the ash, except in the case of some

of the coal-tar colours which are fixed on cotton and linen fibres by means of albumen, or sumach. If albumen has been employed, it may be detected by the ammoniacal vapours, and the peculiar odour given off during the combustion of nitrogenised bodies; whilst, if sumach has been used, a black coloration will be obtained if the fabric be treated with a persalt of iron. This class of colours is now also fixed in steam styles by means of arseniate of alumina, produced on the cloth as follows:—The cloth is first padded in a solution of acetate of alumina, and a properly thickened solution of arsenic acid, glycerine, and the colouring matter printed on, after which the cloth is steamed. If this process has been adopted, the alumina will of course be found in the ash; but to detect the arsenic acid, a portion of the coloured cloth must be heated in a narrow test tube, just sufficiently to char the cloth, the water given off must be removed by blotting paper or a gentle heat, and the charred mass then heated to dull redness, when the arsenic acid will be reduced, and a ring of metallic arsenic will be formed on the cool portion of the tube.

## CHAPTER XII.

### BENZENE, ANILINE, AND MAGENTA.

This and the following chapters are devoted to a consideration of the colouring matters obtained artificially from the products of the destructive distillation of coal, and which are generally known by the name of 'coal-tar colours,' from the circumstance that they are prepared indirectly from coal-tar.

The black, viscid liquid known as coal-tar, is a mixture of a great number of chemical compounds of the most diverse nature, as may be seen by an inspection of the accompanying table, representing the substances which up to the present time have been isolated from it.

| NAME.                       | FORMULA.       | BOILING<br>POINT F. |
|-----------------------------|----------------|---------------------|
| Hexane .....                | $C_6H_{14}$    | 158°                |
| Heptane .....               | $C_7H_{16}$    | 208°                |
| Octane .....                | $C_8H_{18}$    | 251°                |
| Decane .....                | $C_{10}H_{22}$ | about 320°          |
| Amylene.....                | $C_5H_{10}$    | 103°                |
| Hexylene (caproylene) ..... | $C_6H_{12}$    | 149°                |
| Heptylene (œnantlyne) ...   | $C_7H_{14}$    | 205°                |
| Paraffin* .....             | .....          | .....               |
| Benzene .....               | $C_6H_6$       | 178°                |
| Toluene .....               | $C_7H_8$       | 232°                |
| Xylene .....                | $C_8H_{10}$    | 277°                |
| Cumene .....                | $C_9H_{12}$    | 331°                |

\* Solid paraffin is a mixture of the higher members of the marsh gas and olefine series, homologous with hexane and hexylene.



| NAME.                          | FORMULA.        | BOILING<br>POINT F. |
|--------------------------------|-----------------|---------------------|
| Cymene .....                   | $C_{10}H_{14}$  | .....               |
| Naphthalene .....              | $C_{10}H_8$     | 423°                |
| Anthracene .....               | $C_{14}H_{10}$  | about 680°          |
| Chrysene .....                 | $C_{18}H_{12}$  | ?                   |
| Pyrene .....                   | $C_{16}H_{10}$  | ?                   |
| Bisulphide of Carbon .....     | $CS_2$          | 115°                |
| Hydrocyanic acid .....         | $HCN$           | 79°·7               |
| Acetic acid .....              | $C_2H_3O.OH$    | 246°·2              |
| Phenol (carbolic acid) .....   | $C_6H_5.OH$     | 363°                |
| Cresol (cresylic acid) .....   | $C_7H_7.OH$     | 392°                |
| Phlorol (phlorylic alcohol)... | $C_8H_9.OH$     | 428°                |
| Rosolic acid .....             | .....           | .....               |
| Brunolic acid.....             | .....           | .....               |
| Aniline .....                  | $C_6H_7N$       | 360°                |
| Pyridene .....                 | $C_5H_5N$       | 243°                |
| Picoline .....                 | $C_6H_7N$       | 275°                |
| Lutidine .....                 | $C_7H_9N$       | 309°                |
| Collidine .....                | $C_8H_{11}N$    | 338°                |
| Parvoline .....                | $C_9H_{13}N$    | 370°                |
| Coridine .....                 | $C_{10}H_{15}N$ | 412°                |
| Rubidine .....                 | $C_{11}H_{17}N$ | 446°                |
| Viridine .....                 | $C_{12}H_{19}N$ | 484°                |
| Leucoline .....                | $C_9H_7N$       | 455°                |
| Lepidine.....                  | $C_{10}H_9N$    | 500°                |
| Cryptidine .....               | $C_{11}H_{11}N$ | ?                   |
| Pyrrol .....                   | $C_4H_5N$       | 272°                |

This list, however, is far from indicating the whole of the constituents of coal-tar, very many substances undoubtedly exist in it which have not as yet been obtained in a pure state, and submitted to a careful investigation.

One of the most important of the substances above mentioned in connection with the coal-tar colours is aniline,

which, as already noticed (p. 158), was first discovered in 1826, by Unverdorben, amongst the products of the destructive distillation of indigo. He gave it the name of 'crystallin,' from its property of forming crystalline compounds with various acids. Runge subsequently, in 1834, extracted a substance from coal-tar which gave a blue colour with hypochlorite of lime, so he called it 'kyanol.' In 1840, Fritzsche obtained a basic oil by distilling indigo with caustic potash, to which he gave the name of aniline, from the Portuguese word for indigo, *anil*; whilst two years later, in 1842, Zinin prepared a base, 'benzidam,' from nitrobenzene, by the action of ammonium sulphhydrate. It was reserved, however, for Hofmann, in his masterly researches in connection with this subject, to show that all these substances obtained in various ways and from various sources were identical.

In order to separate the various constituents of coal-tar, it is submitted to distillation in cylindrical retorts of cast iron, holding from 1,000 to 2,000 gallons. The more volatile hydrocarbons come over first, but as the distillation proceeds the specific gravity of the product becomes greater, until at last it ceases to float on water: this first portion constitutes 'light oil,' or coal-tar naphtha. On proceeding with the distillation, the boiling point of the distillate rises gradually, and it becomes denser and denser, containing more and more naphthalene and anthracene: this is the 'dead oil,' whilst the residue in the retort is pitch, which is run out whilst hot and in the fluid state. If, instead of running off the pitch at this stage, the fire be urged, a semi-solid mass comes over containing anthracene, chrysene, pyrene, and other hydrocarbons whose nature is unknown; whilst a hard, black, brilliant, rather porous coke is left behind.

In order to obtain aniline directly from coal-tar, the bases, of which it contains about 1 per cent., are extracted

by agitating the coal-oil, boiling between  $300^{\circ}$  and  $450^{\circ}$  F., with hydrochloric or dilute sulphuric acid. After allowing it to stand twenty-four hours, the oil is separated, and the acid liquid agitated with a fresh quantity of oil, repeating the operation until the acid is nearly saturated. The aqueous solution is then distilled with excess of lime or soda, the distillate neutralised by hydrochloric acid, and concentrated by evaporation: on adding lumps of solid caustic soda to this solution, the mixed bases are liberated, and rise to the top of the liquid as an oily layer. In order to separate the aniline, which forms but a small part of the whole, the product is carefully and repeatedly rectified, and the fraction, boiling at  $350^{\circ}$  to  $365^{\circ}$  F., converted into an oxalate; this must be repeatedly crystallised from water and from alcohol, and then decomposed by distillation with an alkali.

Pure aniline may readily be obtained from indigo by mixing it with a concentrated solution of potash, and distilling as long as anything passes over. The product merely requires redistillation to be perfectly pure; the amount being about one-fifth of the indigo originally employed.

It is evident, however, that the direct extraction from coal-oil of the large quantities of aniline required in the manufacture of the aniline colours is too complicated, and its purification too difficult to be of any practical use, whilst to prepare it from indigo would be far too costly. Fortunately however, benzene, which occurs in considerable quantity in coal-tar, can be easily transformed into aniline, by two very simple chemical reactions; in the first of these it is converted into nitrobenzene, which then, by the action of reducing agents, yields aniline.

*Benzene.*—This hydrocarbon was discovered in 1825 by Faraday, but its existence in coal-tar was first pointed out by Hofmann in 1845, and Mansfield succeeded in preparing it in considerable quantity from this source. It is obtained



by the fractional distillation of the light oil after it has been washed with milk of lime and then with water; collecting apart the portion boiling between  $176^{\circ}$  and  $240^{\circ}$  F. This contains almost the whole of the benzene, together with the greater part of the toluene, and after being treated once or twice with 5 per cent. of concentrated sulphuric acid, is again rectified; that portion boiling about  $176^{\circ}$  to  $212^{\circ}$  F., being known in commerce as 'light benzol,' or '90 per cent. benzol'; whilst that from  $212^{\circ}$  to  $250^{\circ}$  F., is known as 'heavy benzol,' or '50 per cent. benzol.' In order to obtain perfectly pure benzene, the commercial article boiling below  $212^{\circ}$  F., should be heated successively with small quantities of sulphuric acid, until it ceases to blacken the latter, and then submitted to fractional distillation. The portion which comes over between  $176^{\circ}$  and  $200^{\circ}$  F., when cooled by a freezing mixture of ice and salt, becomes nearly solid from the separation of crystals of benzene: if the mass be now strongly pressed, melted, and again crystallised once or twice in a similar manner, it will be obtained perfectly pure. Pure benzene may also be readily prepared by the method devised by Mitscherlich in 1835, which consists in distilling a mixture of one part of benzoic acid with three parts of slaked lime.

At the ordinary temperature, benzene is a colourless, mobile liquid, having a somewhat aromatic odour, and at low temperatures solidifies to an almost transparent crystalline mass, which melts at  $50^{\circ}$  F. Its density at  $60^{\circ}$  F. is 0.85, and it boils at  $177^{\circ}.5$  F. It is almost insoluble in water, but is miscible in all proportions with alcohol and ether. It is very inflammable, burning with a brilliant smoky flame.

*Nitrobenzenes.*—By the action of nitric acid on benzene under varying circumstances, it is possible to obtain two nitrobenzenes, in one of which, the mono-nitrobenzene, or as it is generally called, *nitrobenzene*, one atom of the

hydrogen in benzene is displaced by the group  $\text{NO}_2$  forming the compound  $\text{C}_6\text{H}_5\text{NO}_2$ , whilst in *dinitrobenzene*,  $\text{C}_6\text{H}_4(\text{NO}_2)_2$ , two of the hydrogen in benzene are displaced by  $\text{NO}_2$ .

Nitrobenzene was discovered by Mitscherlich in 1834, who obtained it by the action of fuming nitric acid on benzene. As, however, fuming nitric acid of specific gravity 1.5 is costly, it was necessary to seek for some other means of nitrating the benzene. Two mixtures have been employed for this purpose, one consisting of sodium nitrate and sulphuric acid, the other of sulphuric acid, and ordinary commercial nitric acid specific gravity 1.3 to 1.35; the latter is now generally preferred.

The process of converting the benzene into nitrobenzene, is carried on in tall cast-iron pots, about 4 or 5 feet deep and of the same width, provided with a closely-fitting cover, through which passes the shaft of a stirrer, kept in motion by machinery, so that the contents of the vessel may be in constant agitation. Besides the stuffing box for the shaft, there are two other openings in the lid, one to introduce the necessary materials, and the other, furnished with a long pipe, to carry off the nitrous fumes. Both this pipe and also the lid of the apparatus are kept cool by a current of cold water. The entire charge of benzene is first introduced into the apparatus and the agitator set in motion, the mixed acids are then gradually and cautiously run in through a pipe provided for the purpose, but care and experience are required to conduct the operation successfully, as explosions are apt to occur if the acid be added too hastily, or in too large quantities at a time.

After the requisite quantity of the mixed acids has been added, and the reaction is complete, the contents of the iron pot are drawn off by means of an opening at the bottom provided for that purpose. The spent acids run out first, and then the nitrobenzene; the latter is well

washed by agitation with water, and then rendered perfectly neutral by means of a dilute soda solution. If it still contains any unaltered benzene, this may be recovered by distillation.

Pure nitrobenzene is a pale yellow liquid, having an odour strongly resembling that of bitter almond oil, and is very poisonous. Its density at 59° F. is 1.209; it boils at about 420° F., and at 37° F. it solidifies to a mass of pale yellow needles. It is almost insoluble in water, but is readily miscible with alcohol, ether, and benzene.

Dinitrobenzene,  $C_6H_4(NO_2)_2$ , discovered by Sainte Claire Deville in 1841, may be prepared directly from benzene by the action of a mixture of sulphuric acid with fuming nitric acid, or more conveniently, by heating nitrobenzene with a mixture of nitric and sulphuric acids. The crystalline cake which separates on cooling is washed, first with water, and then with a dilute solution of carbonate of soda, and finally crystallised from boiling alcohol.

Pure dinitrobenzene crystallises in long flat prisms, which melt at 176° F., and are very soluble in ether, benzene, and boiling alcohol. It is slightly soluble in boiling water, crystallising out, on cooling, in long slender needles, which are almost colourless.

*Aniline.*—As already noticed, although this base can be obtained from indigo, and also directly from coal-tar, yet, for manufacturing purposes it is universally prepared by the action of reducing agents on nitrobenzene.

Zinin's process consisted in dissolving the nitrobenzene in alcohol, adding ammonia, and saturating with sulphuretted hydrogen. After allowing the solution to stand some time, a large quantity of sulphur is deposited, and the liquid, on examination, will be found to contain aniline. The reaction which takes place may be thus represented:—





Although the reaction is interesting from a scientific point of view, and as being the first by which nitrobenzene was transformed into aniline, it is quite unfit for the preparation of large quantities of material. Béchamp found, however, that reduction took place with far greater facility on substituting acetic acid and iron filings for the ammonia and sulphuretted hydrogen of Zinin.

The apparatus now generally employed in the preparation of aniline consists of a cast-iron cylinder, of the capacity of about 200 gallons, furnished with a tightly-fitting cover in which there are three openings: one for the introduction of the materials; another for the exit of the vapours; whilst the third gives passage to the hollow shaft of the stirrer, set in motion by bevelled wheels. The top of the shaft is ground into an elbow connected with a steam pipe, so that high-pressure steam can be blown through perforations in the stirrer at any desired moment. In order to start the operation, 20 lbs. of acetic acid (specific gravity 1.060), diluted with about six times its bulk of water, are introduced, and then 60 lbs. of pulverised cast-iron and 250 lbs. of nitrobenzene. As soon as the stirrer is set in motion, a brisk reaction ensues. The temperature rises rapidly, and aqueous vapours commence to distil over along with some nitrobenzene. Fresh quantities of iron are introduced from time to time, until the total amounts to 360 lbs., and the distillate is also repeatedly returned to the apparatus. During all this time, and for at least a couple of hours after the introduction of the last quantity of iron, the stirrer must be kept in constant motion. Steam is now blown in through the stirrer, and the aniline distils over along with the aqueous vapours.

In some manufactories the acetic acid, and the whole of the iron, are first introduced into the apparatus, the stirrer is set in motion, and the requisite amount of nitrobenzene is then allowed to flow in gradually. Instead of distilling

the product by steam in the manner described, the semi-fluid mass may be removed from the apparatus, transferred to long narrow iron cylinders, and distilled over an open fire. In this case the aniline always contains some acetanilide. The crude product obtained by Béchamp's process contains acetic acid, acetone, water, and some benzene; to purify it, it is redistilled; acetone passes over first, afterwards benzene, the amount of which should be small, as otherwise it indicates that the operation has not been properly conducted, and then dilute acetic acid. The temperature now rises rapidly, and at 360° F. aniline passes over.

Many other reducing agents have been proposed for the conversion of nitrobenzene into aniline, such as arsenite of sodium, powdered zinc, &c., but none of them have been found so advantageous on a large scale as Béchamp's method. In Kremer's\* process, one part of nitrobenzene is heated in a suitable apparatus with five of water, and two to two-and-a-half of zinc dust. When the reaction is completed, the aniline, amounting to about 65 per cent. of the weight of the nitrobenzene, is distilled off in a current of steam. The reduction both in this case, and also when iron and acetic acid are used, is due to the hydrogen liberated by the action of the metal on water, and may be thus represented :—



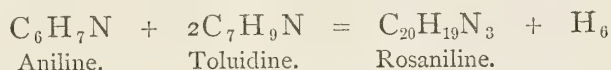
Pure aniline is a colourless, oily liquid, having a peculiar spirituous odour, and pungent, aromatic taste. It is very poisonous. Its specific gravity at 60° F. is 1.020, and when submitted to a low temperature, it forms a crystalline mass, having a melting point of 17°.6 F.: it boils at 360° F. It is only slightly soluble in water, but is miscible in all proportions with ether, alcohol, and benzene.

---

\*Jour. für Prakt. Chem., xc., 255.

With hypochlorite of lime, it gives a bright violet-blue colour, as was first observed by Runge. This phenomenon occurs even with perfectly pure aniline prepared from indigo.

Although magenta and the other colours derived from it are known by the generic term 'aniline colours,' yet it is a curious fact that this dye cannot be obtained from chemically pure aniline. This discovery was made by Hofmann, when endeavouring to ascertain the chemical nature of magenta; he found that pure aniline when heated with arsenic acid in the manner presently to be described did not yield a trace of the beautiful red dye, but, as he knew that in commercial aniline there was another base present called toluidine, he suspected that this, perhaps, might be the true source. On repeating the experiment with pure toluidine, however, equally unsatisfactory results were obtained as with pure aniline; not so, however, when a mixture of the two bases was taken; for on heating one molecule of aniline and two of toluidine with a sufficient quantity of arsenic acid for a short time, the whole solidified to a deep red-coloured mass of nearly pure magenta.

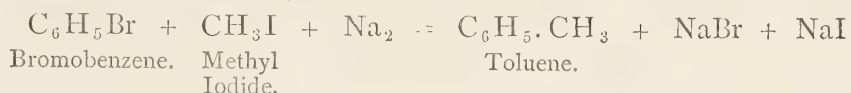


From this it is evident that in order to obtain magenta, which forms the basis of the greater number of the aniline colours, we must have an aniline rich in toluidine. Before proceeding further, therefore, it will be advisable to give a short notice of the latter substance.

*Toluene.*—This hydrocarbon, which is the source of toluidine, has the formula  $\text{C}_7\text{H}_8$ , and may be regarded as benzene, in which one atom of hydrogen is displaced by the methyl group,  $\text{CH}_3$ . In fact, by the action of bromine on benzene, we can displace one atom of hydrogen by that element, forming *bromobenzene*,  $\text{C}_6\text{H}_5\text{Br}$ , and, if we mix



this substance with methyl iodide,  $\text{CH}_3\text{I}$ , and treat the mixture with metallic sodium, the latter combines with the bromine and iodine, and toluene is formed.



This, however, is not the way in which the hydrocarbon is prepared ; it exists ready formed in considerable quantity in coal-tar naphtha, and may be obtained in a tolerably pure state by treating the portion boiling between  $220^{\circ}$  and  $240^{\circ}$  F., with concentrated sulphuric acid, carefully rectifying, and collecting apart the portion which boils at  $232^{\circ}$  F. By these means toluene is obtained as a colourless, mobile liquid, very similar to benzene in appearance and properties, but it does not solidify at  $-4^{\circ}$  F., and it boils at  $232^{\circ}$  F. Its specific gravity at  $68^{\circ}$  F. is 0.875.

*Nitrotoluenes*.—When toluene is boiled with dilute nitric acid it is converted, according to Fittig,\* into *oxytoluic acid*  $C_7H_6O_3$ , whilst fuming nitric acid attacks it with great energy; but the reaction in the latter case differs from what takes place with benzene, inasmuch as not one, but two mononitrotoluenes,  $C_7H_7.NO_2$ , are formed. In order to conduct this operation successfully, fuming nitric acid (S.G. 1.475) is gradually added to carefully cooled toluene, until the latter is completely dissolved; the mixture is poured into a large quantity of water, and the oil which sinks to the bottom thoroughly washed, so as to remove the excess of acid. In order to separate the solid *paranitrotoluene*, Rosenstiehl† distils the mixture, and recrystallises from alcohol the portion passing over above  $446^\circ F.$ , and which solidifies on cooling. Mills finds that if the crude product of the action of nitric acid on pure toluene is distilled in a current of steam, toluene comes over first, and then a mixture of paranitrotoluene with the liquid ortho-

\* Ann. Chem. Pharm., cxx., 966.

† Ann. Chim. Phys., [iv.] xxvii., 433.

nitrotoluene. These two isomerides may be separated very completely by cooling the mixture for half an hour to  $0^{\circ}$  F., and then rapidly filtering with the aid of a water pump; the liquid orthonitrotoluene has a constant boiling point, and no longer yields crystals when again cooled.

Paranitrotoluene forms brilliant white crystals which melt at  $125^{\circ}.6$  F.,\* and boil at  $459^{\circ}$  F. It is almost insoluble in water, but dissolves readily in ether, alcohol, and the liquid modification of nitrotoluene.

*Orthonitrotoluene.*—The liquid modification above mentioned boils at  $432^{\circ}$  F., according to Beilstein and Kuhlberg. It may also be prepared in a pure state from dinitrotoluene by converting it into nitrotoluidine, and then treating this with nitrous acid by Griess's method.

Besides the two nitrotoluenes above mentioned, obtained directly from toluene by the action of nitric acid, a third modification exists called *metanitrotoluene*. It is prepared by converting solid toluidine into the acetyl compound, treating this with fuming nitric acid, and after purifying the product by repeated crystallisation from hot water, decomposing it by boiling it with alcoholic potash. The nitrotoluidine thus obtained, when treated by Griess's process with strong nitric acid saturated with nitrous acid, yields metanitrotoluene. It boils at  $446^{\circ}$  F., and when cooled by a freezing mixture, solidifies to a mass of crystals which melt at  $61^{\circ}$  F. From the results obtained by Wroblevsky,† it would seem that this modification is also present in small quantity in the mixture of nitrotoluenes, obtained directly from toluene by the action of nitric acid.

Besides the mononitrotoluenes, several dinitrotoluenes, and a trinitrotoluene have been obtained, but as they are of no technical interest it is unnecessary to give a description of them here.

---

\* Mills, as the mean of 120 carefully made observations, finds the true melting point to be  $124^{\circ}.54$  F.

† Zeits. Chem., vii., 185.

*Toluidines*.—Three modifications of toluidine,  $C_7H_9N$ , or  $C_7H_7.NH_2$ , are known, corresponding to the three nitrotoluenes; they may be prepared from the latter by treatment with acetic acid and iron in a manner precisely similar to that described when treating of the manufacture of aniline. *Paratoluidine* crystallises from dilute alcohol in large colourless plates, which are only sparingly soluble in cold water, but more readily when it is hot. It is readily soluble in alcohol, ether, benzene, and aniline. It melts at  $113^\circ F.$ , and boils at  $388.5^\circ F.$  *Orthotoluidine* and *Metatoluidine* are oily liquids, and both boil at the same temperature,  $386.5^\circ F.$ ; although the two bases resemble one another so closely, there is a considerable difference in the physical properties of the salts they form with various acids. The toluidine of commerce consists chiefly of a mixture of ortho and paratoluidine in varying proportion, being prepared by Béchamp's process from the mixed nitrotoluenes, obtained from toluene by a method similar to that employed in the manufacture of nitrobenzene.

*Commercial Aniline*.—The liquid known in commerce as aniline is not that base in a pure state, but a mixture consisting in great part of aniline, paratoluidine (solid), and orthotoluidine (liquid) in variable proportions. It also contains small amounts of metatoluidine, nitrobenzene, odorine, &c., but for all practical purposes it may, as just stated, be regarded as a mixture of aniline and toluidine. These anilines are prepared from a portion of the light coal-tar naphtha, boiling between certain temperatures, by treating it precisely in the manner described, first with nitric acid to convert it into the nitro compounds, and then reducing these with iron and acetic acid. It is evident that as the coal-tar naphtha contains variable proportions of benzene and toluene, the product obtained will likewise contain variable proportions of aniline and toluidine. Reimann, in order to distinguish the various qualities of



aniline which come into the market, takes advantage of the different results obtained on submitting them to fractional distillation. For this purpose 100 c.c. of the sample to be tested is placed in a retort furnished with a thermometer, and heated by means of an oil bath. The liquid, as it distils, is received in a narrow, graduated cylinder, and the amount which passes over between every 5° C. (9° F.) noted. In order to obtain standards for comparison, he first distilled a sample of light\* aniline, or 'kuphaniline' as he calls it, then one of heavy aniline or 'baraniline;' afterwards, mixtures of the two in various proportions. The accompanying table shows the results:—

| CENTIGRADE. | K 100 90 85 80 75 60 50 25 0 |     |     |     |     |     |     |    |     |  |
|-------------|------------------------------|-----|-----|-----|-----|-----|-----|----|-----|--|
|             | B 0 10 15 20 25 40 50 75 100 |     |     |     |     |     |     |    |     |  |
| Below 180°  | 8½                           | 7   | 2½  | 5½  | 7   | ... | 7   | 5½ | ... |  |
| 180° - 185° | 54                           | 50  | 29½ | 22  | 5½  | 7   | 4½  | 2½ | 2   |  |
| 185° - 190° | 34                           | 34  | 56½ | 55½ | 55½ | 37  | 7½  | 4½ | 1½  |  |
| 190° - 195° | ...                          | 5   | 7½  | 8½  | 15  | 33  | 42  | 17 | 8   |  |
| 195° - 200° | ...                          | ... | ... | ... | 9   | ... | 19  | 36 | 18  |  |
| 200° - 205° | ...                          | ... | ... | ... | 4½  | 16  | 10  | 16 | 39  |  |
| 205° - 210° | ...                          | ... | ... | ... | ... | ... | 3½  | 8  | 19  |  |
| 210° - 215° | ...                          | ... | ... | ... | ... | ... | ... | 4½ | 7   |  |
| Residue.    | 3½                           | 4   | 4   | 8½  | 3½  | 7   | 6½  | 5  | 5½  |  |

In order to ascertain the nature of any sample, it is only necessary to distil it in the manner described, and compare the results with those in the table.

MAGENTA.—This dye, although it was not the first which was discovered, is, both scientifically and commercially considered, by far the most important, forming

\* The terms light and heavy as here employed are purely conventional, the specific gravity of the so-called light aniline being greater than that of the heavy aniline.

as it does the starting point of the greater number of the other aniline colours. Natanson, in 1856, first noticed that a red colour was produced from aniline, when he was examining the action of chloride of ethylene upon it; two years afterwards, in 1858, Hofmann, when studying the action of tetrachloride of carbon on aniline, observed a magnificent red coloration; but to Verguin is due the first attempt to prepare the colour on a large scale, and to employ it in dyeing. On the 8th of April, 1859, he took out a patent in conjunction with M. M. Renard frères, of Lyons, for the manufacture of the red dye by the action of bichloride of tin on aniline. In this process 20 lbs. of aniline are introduced into enamelled cast-iron pots, capable of holding about 4 gallons, and 14 lbs. of anhydrous bichloride of tin are added in small portions at a time, with constant stirring. As soon as all the bichloride has been added, the mixture is boiled from twenty minutes to half an hour, during which time the yellow fluid mass gradually changes colour, and becomes almost black; the product, which is soluble in water, is now poured out, and employed directly for dyeing; but it does not contain more than 5 or 6 per cent. of rosaniline, the remainder consisting of aniline hydrochloride, and tin salts. The operation should be conducted under a hood, so as to carry off the irritating vapours which are evolved.

The method by which Hofmann obtained aniline red has been employed on the large scale by Messrs. Gerber Keller, of Mulhouse; and also by Messrs. Mounet and Dury, of Lyons. They heat three parts of aniline with one of tetrachloride of carbon, in closed vessels, to  $350^{\circ}$  F., for several hours. A dark brownish-red mass is thus formed, which is purified in a manner similar to that which will be described hereafter, when treating of the arsenic acid process.

The second process for the preparation of magenta was patented in France, on the 29th October, 1859, by Messrs.

Gerber Keller, with whom were associated Messrs. Duran~~E~~ and Schlumberger. Ten parts of aniline are heated in a water bath, and seven or eight parts of mercuric nitrate, dry, and in fine powder, are gradually added, with constant stirring. The mass soon acquires a brown hue, and ultimately becomes of a deep red colour, whilst the mercuric salt is reduced to the metallic state, and is recovered almost entirely as such. Formerly the product, as thus obtained, was sent into the market under the name of 'azaleine,' but it may be purified by any of the usual methods. This process, which is still used to some extent in Germany, is probably the most economical mode of preparing magenta next to the arsenic acid method, but the great risks which the workpeople run from the frightfully poisonous character of the mercury salts and mercurial vapours, render its discontinuance desirable.

The process of Messrs. Lauth and Depouilly consists in heating to about 310° F. a mixture of one part of aniline nitrate, and six or eight of aniline. Great caution must be employed, as otherwise the reaction proceeds with such violence that the mass inflames. After several hours' heating, a deep violet-red product is obtained, containing, besides rosaniline, violaniline, mauvaniline, chrysotoluidine and other colours. The yield of rosaniline is only about 7 or 8 per cent., and the purification is very difficult.

By far the largest part of the magenta made, not only for use in dyeing, but also for conversion into other aniline colours, is prepared by the arsenic acid process devised by Mr. Medlock, and patented by him in January, 1860; a French patent being taken out on the 1st of May, in the same year, by Messrs. Girard and de Laire. The manufacture of magenta, as it is now conducted in the large colour works, is a comparatively simple process; the apparatus employed consisting of a large cast-iron pot set in a furnace, provided with means of carefully regulating



the heat. It is furnished with a stirrer, which can be worked by hand or by mechanical means; the gearing for the stirrer being fixed to the lid, so that by means of a crane, the lid may be removed, together with the stirrer and gearing. There is also a bent tube passing through the lid for the exit of the vapours, and which can be easily connected or disconnected with a worm at pleasure; lastly, there are large openings at the bottom of the pot closed by suitable stoppers, so that the charge can be removed with facility as soon as the reaction is complete. Into this apparatus which is capable of holding about 500 gallons, a charge consisting of 2,740 lbs. of a concentrated solution of arsenic acid, containing 72 per cent. of the anhydrous acid, is introduced, together with 1,600 lbs. of commercial aniline. The aniline selected for this purpose should contain about 25 per cent. of toluidine, for although as already noticed (p. 359), Hofmann has shown that rosaniline is formed from one molecule of aniline and two of toluidine, by the removal of six atoms of hydrogen, yet in practice, it is found that the best results are obtained when a large excess of aniline is employed. After the materials have been thoroughly mixed by the stirrer, the fire is lighted, and the temperature gradually raised to about  $360^{\circ}$  F.: in a short time water begins to distil, then aniline makes its appearance along with the water, and lastly, aniline alone comes over which is nearly pure, containing as it does, but a very small percentage of toluidine; the operation usually lasts about eight or ten hours, during which time about 170 gallons of liquid pass over, and are condensed in the worm attached to the apparatus; of this about 850 lbs. are aniline. The temperature should not exceed  $380^{\circ}$  F. at any period during the operation. When this is complete, steam is blown in through a tube provided for that purpose, in order to sweep out the last traces of free aniline, and boiling water is

gradually introduced in quantity sufficient to convert the contents into a homogeneous liquid. When this occurs, the liquid is run out at the openings at the bottom into cisterns provided with agitators: here more boiling water is added in the proportion of 300 gallons to every 600 lbs. of crude magenta, and also 6 lbs. of hydrochloric acid. The mass is then boiled for four or five hours by means of steam pipes, the agitators being kept in constant motion. The solution of hydrochloride, arsenite, and arseniate of rosaniline thus obtained is filtered through woollen cloth, and 720 lbs. of common salt added to the liquid (which is kept boiling) for each 600 lbs. of crude magenta. By this means the whole of the rosaniline is converted into hydrochloride, which, being nearly insoluble in the strong solution of arseniate and arsenite of sodium produced in the double decomposition, separates and rises to the surface; a further quantity is deposited from the saline solution on allowing it to cool and stand for some time. In order to purify the crude rosaniline hydrochloride, it is washed with a small quantity of water, redissolved in boiling water slightly acidulated with hydrochloric acid, filtered, and allowed to crystallise.

In this process, although the greater part of the colouring matter produced is a salt of rosaniline, other aniline colours are formed at the same time, notably mauvaniline, violaniline, and chrysotoluidine, the amount of which is together almost equal to that of the rosaniline; most of the mauvaniline and violaniline, together with some of the chrysotoluidine, remain in the residues, which are insoluble in water, and are separated by filtration; the remainder of the chrysotoluidine, being much more readily soluble in dilute acids than rosaniline, is found in the acid mother liquors from which the magenta has crystallised. The yield of pure rosaniline hydrochloride in a successfully conducted operation, is from 28 to 30 per cent. of the aniline originally taken.

Besides the method of purification just described in detail there are others, in one of which, by means of an ingeniously constructed apparatus, the crude material may be dissolved and filtered under pressure; in another, the free base is at once extracted in the crystalline state by treating the crude product with boiling milk of lime, or with boiling solutions of baryta or soda.

At present, however, we have only considered the preparation of the hydrochloride of the base, which, although it can be used for dyeing, is not available for the manufacture of many of the other aniline colours. Before, however, proceeding to discuss the methods by which it is treated in order to obtain the free base, which constitutes the starting point of the other forms in which it is used, it will be advisable to glance briefly at its chemical nature.

*Rosaniline.*—Hofmann has conclusively shown that all the varieties of magenta obtained by the different processes above mentioned, and which are so brilliantly coloured, are salts of a colourless base, to which he gave the name of rosaniline, and which has the composition  $C_{20}H_{19}N_3$ . It may readily be obtained by precipitating, with excess of ammonia, a solution of any of the pure crystallised salts of this base met with in commerce. If, for instance, a boiling solution of the hydrochloride be employed, a reddish crystalline precipitate is produced, and the colourless liquid, on cooling, deposits a further crop of crystals of the pure base in colourless needles and plates, having the formula  $C_{20}H_{19}N_3, OH_2$ .

Rosaniline has a bitter taste, and when heated under the surface of boiling water it melts, one thousand parts of the liquid dissolving about three parts; in boiling alcohol, however, it is soluble to the extent of about ten parts in one thousand. It is insoluble in ether and benzene, but very soluble in aniline; when heated above  $430^{\circ}$  F. it is decomposed. Rosaniline is a triamine, and



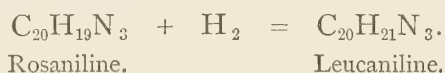
is capable of uniting with either one or three equivalents of an acid to form two series of salts: the members of one of these, the monacid, corresponding to ordinary magenta, are stable crystalline compounds, having a brilliant, green, metallic lustre, and soluble in water and alcohol, forming brilliant red solutions; the other salts, the triacid, are of a deep brownish-yellow colour, and far more soluble in water and in alcohol than the corresponding monacid salts.

The *hydrochloride of rosaniline*,  $C_{20}H_{19}N_3, HCl$ , crystallises in minute rhombic plates, which are only sparingly soluble in water. The triacid hydrochloride,  $C_{20}H_{19}N_3, 3HCl$ , forms brown needles, which gradually lose their acid when heated to  $212^\circ F.$ , being ultimately converted into the monacid salt. The *picrate of rosaniline* forms reddish iridescent needles, which are only very sparingly soluble in cold water. The *acetate of rosaniline*,  $C_{20}H_{19}N_3, C_2H_4O_2$ , which is the finest of all the rosaniline salts, is sometimes met with in brilliant prismatic crystals, half an inch or more in length, and having a beautiful, metallic, golden-green iridescence.

When rosaniline, or any of its salts is heated with water, in closed tubes, to a temperature of about  $460^\circ F.$ , phenol and ammonia are produced; also a substance having the properties of a weak acid, and which crystallises in red needles, of the formula  $C_{20}H_{17}N_2O.OH_2$ . If, however, the water used for solution has been acidulated with hydrochloric acid, the reaction is totally different, the rosaniline being completely resolved into aniline and toluidine; a similar result is produced when it is heated with concentrated hydriodic acid.

As will be seen hereafter, one, two, or three of the hydrogen atoms in rosaniline are capable of being replaced by alcohol radicals, such as methyl, ethyl, phenyl, &c., yielding new bases, the salts of which are blue and violet dyes of marvellous brilliancy and intensity.

When any salt of rosaniline is treated with a reducing agent, it takes up two atoms of hydrogen, and becomes colourless, being transformed into the corresponding salt of a new base, named by Hofmann *leucaniline*.



It may easily be prepared from rosaniline hydrochloride by treating it with metallic zinc and a little hydrochloric acid, or still better, by the action of sulphide of ammonium: a yellow resinous-looking mass is thus formed, which, after being powdered, and thoroughly washed with water, is dissolved in the smallest possible quantity of dilute hydrochloric acid. On adding concentrated hydrochloric acid to this solution, a crystalline precipitate of leucaniline hydrochloride is obtained, which may be purified by repeated solutions in the smallest quantity of water, and reprecipitation by concentrated hydrochloric acid. According to Follenius,\* leucaniline may be prepared from rosaniline by boiling it with zinc dust and water until it is completely decolorised. On cooling, the filtered solution deposits the base in a crystalline state.

All the salts of leucaniline crystallise well, and the free base may readily be obtained from any of them by precipitation with ammonia. It is only sparingly soluble in ether or boiling water, but readily in alcohol or an aqueous solution of leucaniline hydrochloride, crystallising from the latter in splendid crystals. By cautious oxidation it is reconverted into rosaniline.

*Hydrocyanrosaniline*,  $\text{C}_{21}\text{H}_{20}\text{N}_4$ . Hugo Müller observed that on treating rosaniline acetate with potassium cyanide and alcohol, a yellowish-white powder was formed; this may be dissolved in dilute hydrochloric acid, and precipitated by ammonia. As thus obtained, the base forms a white crystalline powder, which is soluble in alcohol. It unites

---

\* *Moniteur Scientifique*, [3] i., 678.

with acids to form colourless salts; the hydrochloride crystallising readily in large monoclinic prisms, which are very soluble in alcohol.

*Preparation of rosaniline and its salts.*—From our knowledge of the chemical nature of magenta, which is rosaniline hydrochloride, we can easily perceive that if we treat it with some basic substance which has a stronger attraction for hydrochloric acid than rosaniline has, the strong base will combine with the acid, leaving the rosaniline in the free state. On a large scale, lime, baryta, and caustic soda are all employed for this purpose, and sometimes ammonia. The magenta is dissolved in a quantity of boiling water sufficient to retain in solution the whole of the liberated base, and a slight excess of the alkali or alkaline earth is added. The mixture is now boiled for several hours, filtered through woollen cloths, and allowed to cool, when the free rosaniline is deposited in magnificent crystals, which are almost colourless.

Unfortunately, however, rosaniline is but slightly soluble in boiling water, so that very large quantities of liquid are required. This difficulty has been obviated, and the operation much facilitated, by the use of an apparatus where the magenta may be decomposed and filtered under a pressure of two or three atmospheres. If the rosaniline hydrochloride is very pure, it is unnecessary to filter; the decomposition being effected by the proper quantity of caustic soda in the course of four or five hours, under pressure, in a boiler furnished with an agitator. On allowing it to cool, the contents are found to be a pulp of colourless crystals, which merely require collecting and washing to be ready to convert into rosaniline salts.

*Acetate of rosaniline*, known commercially as 'roseine,' is one of the most important salts prepared from the base, which for this purpose should be crystalline and free from any excess of alkali. The dry powdered base (200 lbs.)



is introduced into enamelled iron pots, heated to about  $150^{\circ}$  F. by means of a water bath or steam heat, and pure glacial acetic acid (40 lbs.), which must be quite free from sulphurous or sulphuric acids, is gradually added, with constant stirring, until a homogeneous mass is obtained of a deep brick-red colour, and green metallic reflex. Boiling water is now added (50 gallons) to dissolve the acetate, and the mixture boiled for a few minutes, after which it is run into a vat to crystallise. In the course of a few days the salt is deposited in magnificent prisms, about equal in weight to the rosaniline originally employed. Care must be taken that the solution is not boiled for too long a time, as in that case, a change takes place in the solution so that it no longer gives crystals on standing.

Besides those already described, there are other processes by which magenta may be prepared without the use of arsenic.

Messrs. Dale and Caro, in 1860, patented a method of obtaining aniline red, which consisted in heating two parts of aniline, with two of nitrate of lead in fine powder, to a temperature of about  $350^{\circ}$  F.; one part of phosphoric acid was then gradually added to the mixture, and the whole maintained at the above temperature for one or two hours, with constant stirring.

Messrs. Laurent and Casthélaz, have prepared magenta directly from nitrobenzene by mixing it with twice its weight of iron in a fine state of division, and half its weight of concentrated hydrochloric acid. After standing twenty-four hours, the resinous-looking mass, which contains aniline and ferric chloride, is heated, when the ferric chloride reacts on the aniline, producing aniline red. The mass is exhausted with water, and the colouring matter, which was called 'erythrobenzene', precipitated by the addition of common salt to the solution. It was purified by a second solution and precipitation.

More recently Coupier\* has devised a process for the manufacture of magenta without using arsenic acid; he heats a mixture of pure aniline, nitrotoluene, hydrochloric acid, and a small quantity of finely divided metallic iron, to a temperature of about 400° F. for several hours. The pasty mass soon solidifies to a friable mass, resembling crude aniline red; ordinary commercial aniline and nitrobenzene may be substituted for the nitrotoluene and pure aniline in the above process, the products in either case being extracted with water, and the colouring matter precipitated with sodium carbonate. It is identical with ordinary magenta, and may be purified in the usual manner.

Coupier has also prepared another red, which he calls toluidine red, or *rosotoluidine*. This may be made by mixing 95 parts of nitrotoluene with 65 of hydrochloric acid, and then adding 67 parts of crystallised toluidine, and 7 or 8 of ferric chloride. The whole is heated to 375° F. for three or four hours. A product which is very similar, or perhaps identical, is formed, on heating to 310° F. for four hours, 100 parts of liquid toluidine, 35 of hydrochloric acid, and 160 of a solution of arsenic acid, of 75 per cent. Analogous red dyes are obtained when xylydene is substituted for toluidine.

Toluidine red, possesses properties very similar to magenta, but the shade which it gives is somewhat bluer, and more intense. It is also distinguished by its salts being much more soluble in water, and by the greater ease with which, by proper treatment, it yields other aniline colours, especially greens. The proportion of colouring matter obtained from a given weight of the materials is also larger, being about 40 per cent., whilst the yield of aniline red seldom exceeds 30.

Mr. E. C. Nicholson took out a patent in October, 1872,

---

\*Bull. Soc. Chim., [2] xi., 269.

in which he proposed to manufacture magenta by heating a mixture of 3 parts of aniline with 1 of nitric acid specific gravity 1.42, and 1 of hydrochloric acid, specific gravity 1.16, to a temperature of 350°—400° F.

Jegel\* has also employed a very similar process, namely, to saturate 1 part of aniline with nitric acid, then to add 10 parts of aniline saturated with hydrochloric acid, and heat. The magenta is extracted from the melted mass in the usual way.

The xyloidine, boiling at 414° F., prepared from coal-tar naphtha, when mixed with pure aniline and treated with arsenic acid, as in the manufacture of magenta, yields a splendid crimson dye, which rivals that of the rosaniline salts. It is a substantive colour on wool and silk.

According to Rosenstiehl,† crude magenta always contains another base which he calls *pararosaniline*, very similar to rosaniline, and isomeric with it. It appears to be formed from aniline and paratoluidine, and differs from rosaniline in being amorphous. When heated with hydriodic acid, it yields aniline and liquid paratoluidine, instead of aniline and the crystalline toluidine.

Magenta has a most extraordinary affinity for animal tissues, such as silk and wool, which readily take up the colour without the intervention of any mordant; so great is this attraction, that if a large skein of silk be dipped in a weak boiling solution of the red dye, and quickly withdrawn, the water which runs off will be found to be quite colourless, the fibres of the silk removing all the colouring matter from the liquid as it flows between them. This property at first caused great difficulty in applying the colour in silk dyeing, so as to produce an even shade, especially with pale tints. It was found, however, that by dyeing the silk in a weak soap bath, containing compara-

---

\*Chem. Centr., 1874, p. 827.

†Bull. Soc. Chim., [2] x., 192, and xi., 267.

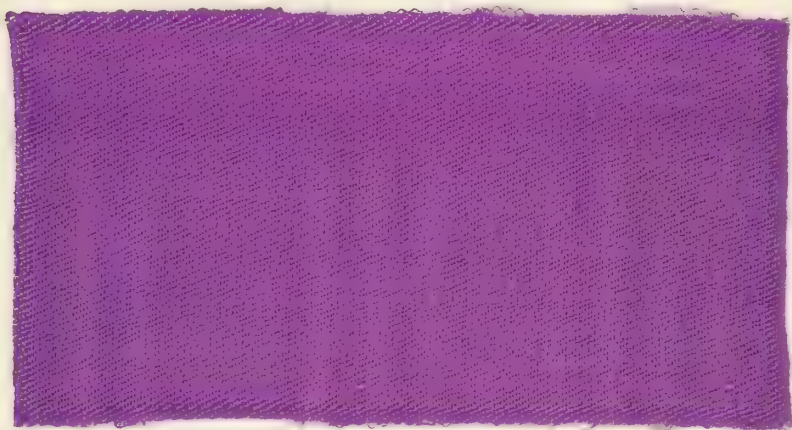


tively little of the colouring matter, this obstacle could be overcome to a great extent: the dyeing proceeds less rapidly, and the face of the silk is kept in good condition. After being thoroughly washed, the dyed silk, which has been rendered soft by the action of the alkali in the soap, is passed through a weak bath of acetic or tartaric acid, to give it the requisite 'scroop', as the peculiar harsh sensation which silk has to the touch is termed. These remarks also apply to the dyeing of silk with many other of the aniline colours, such as Hofmann's violet, Britannia violet, &c.

It is very important, especially in piece dyeing, that there should be no particles of undissolved magenta in the bath, for they would attach themselves to the fabric and produce red spots. On this account it is customary to add the magenta to the bath in a state of solution. Some dyers dissolve it in acetic acid, but this gives it an unpleasant blue shade; a far better method is to grind up the crystals with glycerin, and then boil the mixture with water, and filter; this entirely prevents bronzing on the surface of the tissues, and it has no flattening effect on the colour. Some dyers mix the finely powdered magenta crystals with spirit to a thin paste, and after allowing it to stand for sixteen to twenty hours, mix it with the requisite quantity of hot water, boil for a few minutes, and filter through woollen cloth directly into the dyebeck.

In dyeing woollen goods with magenta, the bath is generally hotter than for silk; and as acids or alkalis injuriously affect the fibre, the solution must be neutral. Considerable care must be taken in order to produce even shades; for this purpose a part only of the total amount of dye to be used is added at first, so as to form a very weak liquor, in which the pieces are rapidly winced. They are then lifted out of the beck, more colour added, the goods re-entered and winced; the operations being repeated until the desired shade has been attained.

A very simple method is sometimes adopted in dyeing woollen goods. A woollen bag filter is fastened at one corner of the dyebeck, the bottom of which dips a few inches into the hot liquor; the quantity of magenta crystals requisite to dye the pieces of the required shade is weighed out, tied up tightly in a piece of flannel, and dropped into the bag filter. Here the magenta slowly dissolves and mixes with the liquor in the dyebeck, which never becomes too strong, an important point; moreover, the solution having to pass through two thicknesses of flannel, all chance of any undissolved particles of the dye coming in contact with the fabric is avoided.



WOOL DYED WITH MAGENTA.\*

Magenta is used not merely alone for rose, pink, and red shades, but also in a variety of compound colours: a beautiful amaranth may be obtained on wool by the following:  $1\frac{3}{4}$  ozs. of magenta are dissolved in 1 lb. of hot glycerin, and the mixture filtered into the dyebeck, in which 8 ozs. of picric acid and 4 ozs. of soda crystals have been

---

\* This, and the nine other beautiful specimens of *woollen* dyed with various coal-tar colours, which occur in this work, have been most kindly furnished by M. Gustave Schaeffer, of Messrs. H. Haefely and Co., Chateau de Pfstadt, near Mulhouse.



dissolved. These quantities give a deep shade with 20 lbs. of wool.

The process of printing silk or wool is extremely simple. It is merely necessary to thicken a filtered solution of the colour, of the proper shade, with gum senegal, print, dry, and steam for about half an hour. The goods are then washed and finished in the usual way.

Although aniline colours have a strong affinity for animal substances, they merely communicate a fugitive stain to vegetable fibres, which is easily removed by washing; moreover, being of a basic nature, the ordinary mordants used for madder and dyewoods, such as alumina and stannic oxide, are found to be of no use. Considerable difficulty, therefore, was experienced at first in their application to the dyeing and printing of cotton.

For dyeing cotton, a mordant is selected which varies according to the circumstances of the case, as to whether the tissue to be dyed consists entirely of cotton, or whether it is a mixed fabric. For pure cotton, either in yarn or woven, it may be prepared as for Turkey red, or it may be treated by the method devised by Perkin and Pullar. It is first steeped for an hour or two in a decoction of galls, sumach, myrobalans, or any other substance rich in tannin, and then after being allowed to drain, worked for an hour or two in a weak solution of sodium stannate. It is finally passed through a bath of alum or dilute sulphuric acid, and then rinsed in cold water. Cotton, thus prepared, has a pale yellow colour, and readily takes up the magenta when worked in a cold bath of that dye. Cotton may also be dyed a very good and fast colour, by working it in a solution of lead sub-acetate, and then in a weak soap bath.

In piece dyeing, where the warp is cotton, and the weft woollen, the process of mordanting is slightly varied. The material is first soaked in an infusion of a tannin matter,



and then winced in a bath of tin crystals. After being washed, it is ready for the dyebeck.

Calico may be printed with magenta, or any of the aniline colours, by mixing the solution with albumen or casein, and thickening it in the usual way with starch or gum. The process of Messrs. Perkin and Schultz, also gives excellent results, the colour is first printed on with a thickened mixture of sodium arsenite, and aluminium acetate, the proportions being—

1 litre of acetate of aluminium, at 10° B.

80 grammes of arsenite of sodium.

16 „ magenta.

The pieces are then steamed for an hour, soaped, and washed in pure water: by these means, very brilliant shades are obtained with nearly all the aniline colours.



MAGENTA PRINTED ON COTTON.\*

A fine purple may be obtained on cotton, by steeping it for a couple of hours in a hot bath containing 3lbs. of turmeric, and 1lb. of sumach. 1lb. of sulphuric acid is then added, the yarn worked in the mixture, taken out, and

\*This, and the seven other splendid samples of aniline colours printed on calico, which are interspersed throughout this portion of the work, have been generously placed at our disposal by M. Horace Koechlin, of Wisserling, Alsace.

washed. Cotton thus mordanted, has a yellow colour, and acquires a fine purple shade when worked in a magenta bath.

ADULTERATION OF MAGENTA.—The presence of any of the foreign colours, violaniline, mauvaniline, or chrysotoluidine, may be readily ascertained by dissolving the suspected sample in the smallest possible quantity of alcohol, diluting with rather more than its own bulk of water, and then putting a drop of the liquid on a piece of white blotting paper. The spot formed by the capillary action of the paper will present concentric circles of different tones of colour if the magenta is not pure. This simple method may also be applied to the examination of aniline blues and violets.

As in the case with the madder dyestuffs, one of the best methods of testing magenta, both for the purity of tone and also for the amount of colouring matter, is to make a comparative dyeing experiment with the sample under investigation, and with one of known purity, using white woollen yarn.

Crystallised magenta is sometimes adulterated to a large extent with sugar which has previously been dyed with magenta. On spreading out such a sample on a sheet of white paper in the sunshine, the larger crystals of dyed sugar may readily be detected by their colour being paler at the edges. When picked out and washed with alcohol, they become colourless, and the odour of caramel which is produced when they are heated is sufficient to identify them. The amount of this adulteration may be determined by washing a weighed quantity of the sample with absolute alcohol until colourless, or nearly so, and then drying and weighing the residue, or more accurately by dissolving a weighed portion of the dye in hot water, and precipitating the rosaniline as picrate by means of picric acid. The clear yellow solution is now precipitated with



basic acetate of lead, filtered, the excess of lead thrown down by sulphuretted hydrogen, and the amount of sugar present estimated by means of the polariscope.

There are several other aniline reds met with in commerce besides magenta, the most important of which are safranine, geranosine, ponceau, and Ulrich's scarlet.

SAFRANINE, OR SAFFRANINE, is a bright rose-coloured dye, which, according to Mené, is prepared commercially by treating heavy aniline oils successively with nitrous acid and arsenic acid, or two parts of the aniline may be heated with one of arsenic acid and one of an alkaline nitrate for a short time, to  $200^{\circ}$  or  $212^{\circ}$  F. The product is extracted with boiling water, neutralised with an alkali, filtered, and the colour precipitated with common salt. It is met with both in the state of paste, and also as a yellowish-red powder, which contains the hydrochloride of the base mixed with calcium carbonate and common salt. On boiling this with water, filtering, and acidulating the filtrate with hydrochloric acid, a crystalline substance separates on cooling, which, after repeated crystallisation in a similar manner, no longer leaves any residue on ignition. The addition of hydrochloric acid to the filtrate is necessary, as otherwise it is found to lose acid by repeated crystallisation, and to become much more soluble.

Pure *safranine hydrochloride*,  $C_{21}H_{20}N_4, HCl$ , forms thin reddish crystals which are soluble in water and in alcohol, yielding intensely yellow-red solutions. The free base safranine may be obtained from this by decomposing the solution with silver oxide, and evaporating the deep-red liquid. It forms reddish-brown crystals, which are very soluble both in alcohol and in water.

Hofmann and Geyger,\* who have carefully investigated the subject, find that safranine cannot be prepared either from pure aniline or pure crystalline toluidine, or from a

---

\* Deut. Chem. Ges. Ber., v. 526.

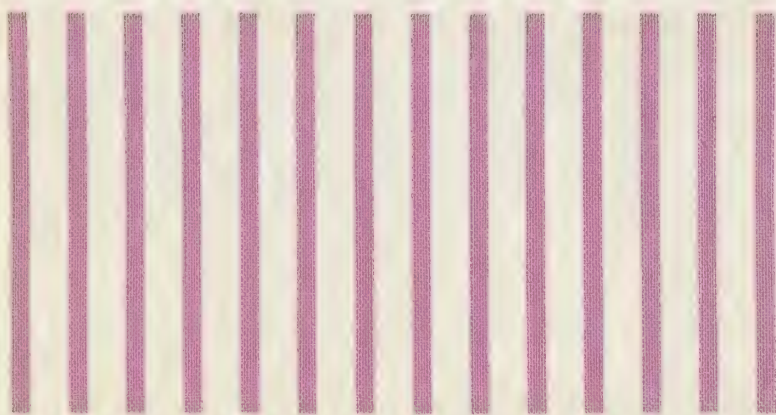


mixture of the two, but that it is derived from the liquid toluidine, boiling at 389° F., the reactions being as follow:—



The action of nitrous acid first produces the compound  $\text{C}_{21}\text{H}_{24}\text{N}_4$ , which is then converted by the action of the oxidising agent into safranine. They find, however, that when arsenic acid is employed for this latter purpose, the safranine is mixed with a large amount of secondary products. This may be avoided to a great extent by substituting chromic acid for arsenic acid as the oxidizing agent.

The most characteristic reaction of safranine is, that when concentrated sulphuric acid is gradually added to its solutions, the colour first changes to violet, and then passes successively to blue, dark green, and light green; on now diluting the solution with water, the same changes of colour will be observed, but in the reverse order.



SAFRANINE.

Safranine may be printed by thickening the paste with twenty parts of a mixture consisting of—

|                                   |          |
|-----------------------------------|----------|
| Acetate of alumina standard ..... | 1 gallon |
| Water .....                       | 1 „      |
| Starch .....                      | 2 lbs.   |

Boil, and when cold add 1 pint of arsenic standard.

The acetate of alumina standard is the clear liquid obtained on precipitating a solution of 5 lbs. of alum in 2 gallons of water, with 6 lbs. of lead acetate, and allowing to settle.

The arsenic standard is made by boiling 4 lbs. of arsenious acid (white arsenic) in 1 gallon of glycerin, until dissolved, and then filtering.

After printing, the goods are steamed for half an hour.

Safranine is now superseding safflower, or carthamine, as a red dye for silk. It requires no mordant.

GERANOSINE.—This is a beautiful ponceau red, obtained from rosaniline by a process devised by Luthringer. To prepare it 2 lbs. of magenta are dissolved in 200 gallons of boiling water, and as soon as it has cooled down to 113° F., a solution of 9 lbs. of barium or calcium nitrite in 7 gallons of water is poured in (peroxide of barium may be substituted for the nitrite if thought desirable). As soon as the two liquids are thoroughly mixed, 20 lbs. of concentrated sulphuric acid are added. The liquid instantly becomes yellow, and in a few moments colourless; it is now filtered from the precipitated barium sulphate and gradually heated to the boiling point. The liquid, which thus acquires an intense red colour, is boiled for two or three minutes, allowed to cool, and the colouring matter precipitated by common salt.

PONCEAU.—This is a colour manufactured by Messrs. Brooke, Simpson, and Spiller, by a secret process. It is a very brilliant red, and retains its colour when seen by artificial light. It dyes wool and silk without a mordant, the only precaution necessary being to add the colour very gradually to the bath, and so work slowly up to the required shade. The addition of a little ammonia to the bath varies the hue.

CERISE.—This is the name given to a colour manufactured by Knosp, of Stuttgard, from magenta residues,

and is probably a mixture of rosaniline and chrysotoluidine. It is thrown down on adding carbonate of soda to the mother liquors obtained in the manufacture of magenta, after that colour has been precipitated by common salt. It dyes wool and silk scarlet shades.

ULRICH'S SCARLET.—This is a compound obtained by the partial oxidation of magenta. To prepare it, a solution of three parts of lead nitrate, dissolved in the smallest possible quantity of boiling water, is mixed with four parts of powdered rosaniline acetate, and the whole evaporated to dryness at a gentle heat. The dry mass is now heated gradually to a temperature varying from 300° to 400° F., when it becomes violet. The product, as soon as it is cold, is extracted by boiling with very dilute sulphuric acid. The solution is then neutralised, filtered boiling hot, and the colour precipitated in the usual way with common salt.

This scarlet yields a rose-red dye when heated under pressure with alcohol, and methyl or ethyl iodide, as in the process for preparing Hofmann violet. It is purified in a similar manner to that colour.



## CHAPTER XIII.

### ANILINE VIOLETS.—ANILINE BLUES.

ANILINE VIOLETS.—The most important of these from a scientific and historical point of view is mauve, or aniline purple, discovered by Mr. W. H. Perkin, and patented by him in August, 1856.\* Not only was this the first dye made from aniline which received any practical application, but the brilliancy and beauty of the new colour, as compared with those hitherto obtained, excited universal attention, so that the investigation of the nature of the aniline derivatives was pushed forward with great vigour. The result was the establishment of an entirely novel branch of manufacture, which has since developed to such an enormous extent, not only in the production of the various 'coal-tar colours,' but, as we have already seen, in the artificial production on a manufacturing scale of alazarin, a dye which was formerly only obtained from the root of the madder and other plants.

Mr. Perkin's own account of his discovery, as related before the Society of Arts, is as follows:—

"Chemists have always been desirous of producing natural organic bodies artificially, and have, in many instances, been successful. It was whilst trying to solve one of these questions that I discovered the 'mauve.' I was endeavouring to convert an artificial base into the natural alcaloid quinine, but my experiment, instead of yielding the colourless quinine, gave a reddish powder. With a desire to understand this peculiar result, a different base of more

---

\* No. 1984.

simple construction was selected, namely, aniline, and in this case I obtained a perfectly black product: this was purified and dried, and when digested with spirits of wine gave the mauve dye."

This dye is prepared by the action of oxidising agents on an aqueous solution of a salt of aniline. The nature of the aniline is a very essential point, for it has been found that, that which gives the best results for magenta is not at all suitable for the production of mauve. The process generally adopted for its manufacture is that originally devised by Perkin:—108 lbs. of sulphuric acid are diluted with 4 lbs. of water, and when cool the mixture is gradually poured into 200 lbs. of suitable heavy aniline, with constant stirring. When all the acid has been added, the mixture is heated, and stirred, so as to render it homogeneous, and then allowed to cool; 280 lbs. of potassium dichromate are then dissolved in the smallest possible quantity of water, and stirred into the mixture, allowing the whole to stand twenty-four hours. At the expiration of this time, the liquid, which at first was turbid, has become quite clear, the impure mauve being found at the bottom of the vessel as a black precipitate. The supernatant liquor is now drawn off, and the precipitate thoroughly washed three or four times by stirring it up with boiling water; it is afterwards washed with water acidulated with sulphuric acid, and finally with cold water. The colouring matter is extracted from the precipitate by boiling it with water for about three hours, decanting and filtering: the process being repeated until no more colouring matter is dissolved. An alkali, or alkaline carbonate is added to the aqueous solution thus obtained, in order to precipitate the base *mauveine*, which is collected, washed with warm water, and dissolved in the requisite quantity of acetic acid. In order to obtain the base in a tolerably pure state, the processes of solution, precipitation, and washing must be repeated several times.

When mauve was first manufactured, the crude product was purified by washing and drying it, and then treating it in closed vessels with boiling coal-tar naphtha to remove resinous impurities. After this, it was exhausted with dilute spirit, the spirit distilled off, and the aqueous solution of the colouring matter which was left, filtered and precipitated with caustic soda. The loss of valuable solvents, and the danger in manipulating with large quantities of inflammable liquids caused this process to be superseded by that just described.

On dissolving the purified mauve in boiling alcohol and acetic acid, a solution may be obtained which deposits the acetate of mauveine in the crystalline state. It may be purified by one or two crystallisations, when it has a splendid green metallic lustre. It is occasionally met with in commerce in this state, but more generally in paste, or in solution, as the crystals are costly, and do not offer any corresponding advantage to the consumer.

The base *mauveine*,  $C_{26}H_{24}N_4$ , unlike rosaniline, is not colourless, but of a dingy violet colour. It may readily be obtained by dissolving a pure salt of the base in boiling alcohol, and adding a slight excess of an alcoholic solution of potash: on cooling, it is deposited in black glistening crystals not unlike specular iron ore in appearance. Mauveine is a very powerful base, readily expelling ammonia from its salts when boiled with them. It is almost insoluble in benzene, and in ether, but dissolves to some extent in alcohol, forming a dingy violet-blue solution: the addition of an acid immediately changes this to a deep purple, resulting from the formation of a salt of mauveine. The sulphate and hydrochloride of mauveine may both be obtained in the crystalline state; the former is the original aniline purple, formed by the action of potassium dichromate on aniline sulphate. The salts of mauveine are generally very hygroscopic; they are only slightly soluble



in cold water, somewhat more so in boiling water, and readily soluble in alcohol and wood spirit. When submitted to the action of nascent hydrogen, mauveine takes up hydrogen, and becomes converted into a new base, the salts of which are colourless, or nearly so. This may be well illustrated by boiling an alcoholic solution of mauve with a few strips of zinc in a tube, which is imperfectly closed, when the dark purple of the solution gradually changes to yellow. On exposure to the air, however, it rapidly acquires its original purple colour.

Perkin has found that in the formation of mauve or aniline purple, there is always a small quantity of a second colouring matter produced, which gives rich crimson or rose shades, similar to those from safflower. It occurs, however, but in small quantity. When pure, it crystallises in small prisms possessing a beautiful golden-green lustre. It is soluble both in water, and in alcohol, yielding solutions remarkable for their fluorescence, so much so, that in certain lights the clear transparent liquid appears turbid.

*Phœnicine* is a ponceau red dye, discovered by Willm in 1861, who prepared it by boiling a solution of mauveine in acetic acid, with barium peroxide, until the red colour was fully developed. The liquid is then poured out and carefully neutralised with carbonate of soda. The colour may be thrown down from the filtered liquid by means of common salt.

It is not improbable that this red is identical with that described by Delvaux, as obtained by the action of chromic acid on aniline: 1 part of chromic acid is dissolved in 20 of water, and 1 part of aniline is added. After standing for twenty-four hours, the black precipitate which is produced is exhausted with boiling water, and the filtered solution rendered alkaline with ammonia. Aniline purple is then thrown down, whilst a red colouring matter remains in solution.

Mauve has also been manufactured in France by the action of hypochlorite of lime on a solution of a salt of aniline. Perkin has investigated this reaction, and finds that the blue colour observed many years ago by Runge, on adding a solution of hypochlorite to one of aniline, is not due to mauve, but to a distinct substance of a blue colour. On mixing solutions of aniline hydrochloride and calcium hypochlorite (chloride of lime) the solution gradually becomes turbid from the formation of a finely divided indigo-blue precipitate. On adding common salt this new substance is precipitated. It is, however, very impure, and requires treatment with ether or benzene to remove brown-coloured resinous substances. Runge's blue, as thus prepared, is a solid substance, which dissolves in alcohol with a fine blue colour, and is capable of dyeing silk of a blue colour; it is, however, very unstable, the colour of the alcoholic solution changing to purple in a day or two at the ordinary temperature, and immediately if heated. The same effect is observed on the dyed fabric. In the process of manufacture adopted in France, the product is boiled so as to convert it into mauve. In Messrs. Depouilly and Lauth's patent, taken out in June, 1860, the precipitate formed by the addition of a solution of chloride of lime to a solution of aniline hydrochloride was washed with acidulated water, dissolved in concentrated sulphuric acid, and reprecipitated by water. The amount of product obtained by this method is said to be larger than when Perkin's process is employed, but the shades obtained in dyeing are not so pure.

About this time several other processes were patented for the production of mauve by the action of various oxidising agents on aniline. In January, 1860, Mr. Kay proposed to manufacture mauve by heating a solution of aniline sulphate with manganese peroxide (black oxide of

manganese) to  $212^{\circ}$ , and, when the reaction was complete, precipitating the colour with an alkali.

Mr. C. Greville Williams also patented the production of a purple dye by oxidising aniline with potassium permanganate; and in the latter part of the year 1859 Mr. David Price took out a patent for the manufacture of aniline purple, by boiling a solution of one molecule of aniline sulphate with two of lead peroxide; the solution of the colouring matter thus obtained was filtered, concentrated by evaporation, and, after a second filtration, precipitated by an alkali. According to Dollfus,\* Messrs. Frank & Co., of Lyons, and Messrs. Grüner & Co., Glauchau, in the year 1859, succeeded in obtaining a reddish-violet colour by treating a solution of magenta in wood spirit with potassium dichromate and sulphuric acid. This process, which was at first a secret, afterwards became generally known. The nature of the reaction which takes place in the production of this colour has not been ascertained, but it is well known that if magenta is dissolved in wood spirit it yields on fabrics a much bluer shade than when water or alcohol is employed as the solvent.

In May, 1860,† Messrs. Dale and Caro patented a process for preparing aniline purple, differing from that of Mr. Perkin, the oxidising agent employed being cupric chloride. One equivalent of a neutral salt of aniline is mixed with six equivalents of chloride of copper, dissolved in water (thirty times the weight of the aniline salt), and the whole boiled for three or four hours. The dark coloured precipitate is purified by processes similar to those employed in treating the product obtained by Perkin's method. A mixture of common salt and sulphate of copper, in equivalent proportions, may be substituted for the cupric chloride.

In January, 1861, M. Girard took out a patent for

---

\* Wagner's Jahresbericht, xx., 794.

† No. 1307.



preparing '*Violet Imperial*' by heating a mixture of equal weights of magenta and aniline to 330° F. for several hours. The purple-coloured mass after being washed with water and hydrochloric acid, to remove any unaltered aniline or magenta, is ready for use. It is readily soluble in alcohol, acetic acid, and wood spirit. This dye, which was long regarded as a compound of magenta and aniline blue, has been shown by Hofmann to consist of a mixture of salts of *monophenylrosaniline*,  $C_{20}H_{18}(C_6H_5)N_3$ , and *diphenylrosaniline*,  $C_{20}H_{17}(C_6H_5)_2N_3$  identical with those obtained in the manufacture of aniline blue, when an insufficient quantity of aniline has been employed.

*Monophenylrosaniline* salts are of a reddish-violet colour, and may be prepared as follows: 80 lbs. of aniline, and 20 of rosaniline sulphate or hydrochloride, both in a perfectly dry state, are heated in an apparatus similar to that employed for the manufacture of aniline, gently for the first half-hour, after which the temperature is raised, but should never exceed 375° F. The progress of the action must now be tested every five minutes by withdrawing a small portion of the material by means of a glass rod, and transferring it to a white porcelain plate, where it is mixed with a little alcohol and acetic acid. The operation is interrupted immediately the colour is observed to be of a pure red-violet tint; and as soon as the contents of the vessel are cool enough, they are poured in a very thin stream into a vessel containing an acidulated solution of common salt, which is kept violently agitated by mechanical means. The impalpable powder thus obtained is purified by washing it thoroughly, first with a similar solution, and then with pure water; after being pressed and dried at a low temperature, it is fit for the market. Another method of purification consists in pouring it into benzene, dissolving the precipitate in the smallest quantity of concentrated hydrochloric acid, and then largely diluting with water: the violet is thus

precipitated, whilst the unaltered magenta remains in solution.

*Diphenylrosaniline* salts are of a much bluer tinge than the corresponding monophenylated compounds. The method of preparation is very similar, but the time of heating is longer, and rosaniline acetate is employed instead of the sulphate or hydrochloride; 20 lbs. of the acetate to 40 of aniline, giving good results. The product is poured into about 80 gallons of alcohol, which is then acidulated with hydrochloric acid, and the violet dye precipitated by means of a saturated aqueous solution of common salt. It now merely requires to be washed once or twice with acidulated water, and finally with pure water.

In preparing these phenyl violets, Levinstein employs 100 parts of magenta, 100 of aniline, and 25 of acetate of soda, for the red shades; and 3 parts of aniline to 1 of magenta for the blue shades. In the production of very blue violets, soap is often used, the heat being continued for a considerable time:—300 parts of magenta, 100 of aniline, 75 of sodium acetate, and 66 of white curd soap is a mixture which gives good results. The excess of aniline may be removed by boiling the product with very dilute hydrochloric acid, and the dye which floats on the surface, is skimmed off, washed, dried, and powdered.

These violets are soluble in alcohol, acetic acid, and glycerin, but their employment is comparatively limited since the discovery of the Hofmann and Paris violets, which are methylated or ethylated rosaniline salts.

Mr. G. C. Nicholson in 1862, took out a patent for the preparation of '*Regina purple*,' by the following process: "I take red dye, such as is made from aniline or its homologues and, without the admixture of either aniline, or its homologues, I heat it carefully, in a suitable apparatus, to a temperature by preference between 390° and 420° F. The substance quickly assumes the appearance of a dark



semi-solid mass, the red dye being transformed into a dark substance with evolution of ammonia. The mass I prefer afterwards to extract with acetic acid, using a quantity of acid about equal in weight to the amount of the red dye treated, and this acid I dilute with enough alcohol to make a dye of convenient commercial strength; the solution obtained is of a deep violet or purple colour, and may be used directly for dyeing purposes."

*Kopp's violet* is prepared by grinding up rosaniline tannate to a paste with three or four times its weight of wood spirit, and then adding about one-twentieth of its volume of nitric or hydrochloric acid, or better, of a saturated alcoholic solution of hydrochloric acid. The red colour of the mixture gradually acquires a violet tinge, which, on standing, becomes more and more defined, and then passes into a nearly pure blue. By properly regulating the amount of acid, any desired shade may be obtained. When the product is dry, it merely requires washing with water to remove the excess of acid in order to be ready for use. It should be dissolved in alcohol, or wood spirit, and the liquid diluted with water.

A violet may also be obtained mixed with Prussian blue and other extraneous matters, by boiling for half an hour a mixture of equal equivalents of potassium ferrocyanide (red prussiate) and a salt of aniline, dissolved in 20 parts of water. Potassium ferrocyanide remains in solution, and a precipitate is produced, which is first treated with coal oil to remove brown resinous matters, after which the violet colouring matter may be extracted by boiling alcohol.

*Mauvaniline* and *Violaniline*. It has been already noticed (p. 367) that in the preparation of magenta three other colouring matters are produced, namely, mauvaniline, violaniline, and chrysotoluidine, which in great part remain undissolved when the crude magenta is treated with water. These residues, which amount to nearly one-half of the



total products of the reaction, were formerly regarded as useless; but Paraf, and subsequently Girard and De Laire, have succeeded in separating the bases, and rendering them available for dyeing purposes. In order to effect this, the insoluble residue is first boiled with caustic soda, in order to obtain all the bases in the free state; these are now treated with dilute hydrochloric acid, which dissolves the chrysotoluidine and mauvaniline, and leaves the violaniline. On adding common salt to the hydrochloric acid solution, mauvaniline hydrochloride is precipitated, whilst chrysotoluidine salt remains in solution. Mauvaniline may be obtained in crystals having the formula  $C_{19}H_{17}N_3, OH_2$ , which are insoluble in water, but soluble in alcohol, ether, and benzene. Its salts are soluble in water, and yield fine red-purple tints on fabrics. The colours produced by violaniline are dull and little used.

*Methyl and ethyl-rosanilines.*—It has been already stated that Hofmann, when engaged in investigating the nature of rosaniline, discovered that it was a triamine in which there were three equivalents of hydrogen capable of being replaced by alcohol radicals. In fact, he found on heating it with excess of ethyl iodide for some hours to  $212^\circ$  in closed tubes, that a magnificent purple substance was produced, which was the iodide of a new base, *triethylrosaniline*  $C_{20}H_{16}(C_2H_5)_3N_3$ , or rosaniline  $C_{20}H_{19}N_3$ , in which three of the hydrogen had been replaced by three ethyl groups,  $C_2H_5$ . By varying the circumstances of experiment, instead of three of the hydrogen being replaced by ethyl, dyes may be obtained having two, or only one, replaced by ethyl; moreover, by substituting methyl iodide for ethyl iodide, corresponding methyl compounds may be prepared. In this way Hofmann violets are obtained of different shades, varying from RRR, the very red, which is principally a salt of monomethylated rosaniline  $C_{28}H_{18}(CH_3)N_3$ , to BBB, the bluest shade.

*For the red-violet RRR.*

|                                      |         |
|--------------------------------------|---------|
| Rosaniline .....                     | 20 lbs. |
| Alcohol .....                        | 200 „   |
| Hydrate of potassium or sodium ..... | 20 „    |
| Iodide of methyl or ethyl.....       | 16 „    |



HOFMANN VIOLET, RRR.

*For a blue-violet B.*

|                                      |         |
|--------------------------------------|---------|
| Rosaniline .....                     | 20 lbs. |
| Alcohol .....                        | 200 „   |
| Hydrate of potassium or sodium ..... | 20 „    |
| Iodide of methyl .....               | 10 „    |
| Iodide of ethyl .....                | 10 „    |



HOFMANN VIOLET, B.



# MANUFACTURE OF HOFMANN VIOLET, 395

*For a bluer shade BB.*

|                                     |         |
|-------------------------------------|---------|
| Rosaniline.....                     | 20 lbs. |
| Alcohol .....                       | 200 „   |
| Hydrate of potassium or sodium..... | 20 „    |
| Iodide of methyl .....              | 40 „    |

These violets are now made in enamelled iron autoclaves of a capacity of about 18 or 20 gallons, and capable of sustaining a pressure of 300 to 400 lbs. on the square inch. They are fitted with a thermometer and a pressure gauge, and are heated by means of a water bath or steam jacket. The preceding are the proportions given by Girard and De Laire.

The rosaniline and a portion of the alcohol are introduced into the apparatus, and heated with part of the iodide; the potash in alcoholic solution, and the iodide being added alternately, in successive portions, during the operation; this takes about two hours, the temperature being 240° to 265° F. When the required shade is attained, the contents of the boiler are drawn off and purified. With methyl iodide the product is bluer and more soluble in water than when the corresponding ethyl compound is employed.

In order to purify the crude product and recover the iodine, the colouring matter, after the separation of the excess of alcoholic iodide by distillation, is treated with a hot alcoholic solution of soda in an apparatus provided with a cohabator and an agitator. The precipitated base, after being thoroughly washed with boiling water, is treated with sulphuric, hydrochloric, or acetic acid, and the resulting salt dissolved in boiling water and precipitated with common salt or sodium acetate. These aniline violets are readily soluble in alcohol and in water, and may be obtained in the crystalline state.

Although the free base, rosaniline, is generally used in the preparation of these colours, it is not absolutely essential.



Very good results may be obtained by heating together rosaniline acetate, methyl iodide, and alcohol, or wood spirit: in fact, Hofmann's violets are frequently made in this way in Germany. The action, however, takes place with less facility, so that a higher temperature and a longer time are required.

The Hofmann violets are remarkable for the brilliancy of their colour, but unfortunately they do not resist the action of light so well as many other of the aniline colours—this is especially the case on cotton. It is generally the case that aniline colours resist light better when applied to animal fibres, such as silk or wool.

In the formation of these colours it will be observed that as more and more of the hydrogen in the red magenta is replaced by methyl or ethyl, the bluer is the shade of violet produced. With mauve, however, the effect is exactly the reverse, the shade produced by the salts of the new ethylated or methylated base being redder than that of the original dye. A colour intermediate between aniline purple and magenta, and known as 'dahlia,' is prepared in a similar manner to the Hofmann violets by the action of alcohol and iodide of ethyl on mauveine. This colour possesses the same character for fastness as mauve, but unfortunately it is rather expensive, and therefore is not used very extensively.

Instead of preparing magenta by the action of oxidising agents on a mixture of aniline and toluidine, and then replacing one or more equivalents of the hydrogen in this base by an alcohol radicle, such as ethyl or methyl, in order to obtain these violet dyes; we may first introduce the alcohol radicle into the aniline and toluidine, and then submit the methylaniline and methyltoluidine thus formed to the action of oxidising agents. It is in this way that the so-called '*Paris violet*' is prepared.

The first step in the manufacture of this dye is the pre-

paration of *methylaniline*, which in the pure state has the composition  $C_7H_9N$  or  $C_6H_6(CH_3)N$ , being aniline in which one atom of hydrogen is replaced by the methyl group  $CH_3$ . As produced on the large scale, however, from commercial aniline, which is a mixture of aniline and toluidine, it is, of course, a mixture of methylaniline and methyltoluidine. Both the iodide and bromide of methyl combine with aniline most energetically, producing methylaniline hydriodide, or hydrobromide, from which the free base may be liberated by means of a caustic alkali. The high price of both bromine and iodine, however, is an obstacle in the way of the adoption of this process, and other methods have been devised by which the base may be more conveniently obtained. On heating to about  $550^\circ F.$ , for twelve hours, a mixture of 60 or 80 parts of wood spirit, and 100 of aniline hydrochloride, the latter becomes converted into the corresponding methylaniline salt. A similar result is produced by heating to  $570^\circ F.$ , 100 parts of aniline, 80 of wood spirit, and 100 of ammonium chloride. The aniline may also be treated with methyl nitrate, or methyl chloride, either at the ordinary temperature, or at  $212^\circ F.$  under pressure. In any case the salts produced are decomposed by caustic soda, and the oily mixture of methylaniline and dimethylaniline is distilled in a current of steam, and then rectified in an oil bath, collecting apart the portion which boils above  $410^\circ F.$

The Paris violet was discovered by M. C. Lauth, but the processes have since been much improved by Messrs. Poirrier and Chappat. Lauth heats salts of methylaniline and dimethylaniline, such as the hydrobromide or hydrochloride, either with sand, or with certain oxidising agents such as cupric nitrate or chloride, mercuric acetate, &c. Poirrier's process consists in gradually adding 5 or 6 parts of anhydrous stannic chloride to 1 of methylaniline in successive portions, and then heating the mass to  $212^\circ F.$  for

several hours, until it becomes hard and brittle. When cold it is washed and boiled with a solution of caustic soda, which removes the tin, and leaves the base in a free state. This is then taken up with the equivalent quantity of hydrochloric or acetic acid, and the solution evaporated to dryness at a gentle heat. A bronzed mass is left, which is very soluble in water, alcohol, and acetic acid. Instead of stannic chloride other oxidising agents may be used, as is shown by the following methods which have been proposed:—Heat to  $212^{\circ}$  F. 100 parts of methylaniline, 80 of potassium chlorate, and 20 of iodine; the reaction is sluggish, and takes several days before it is complete. Heat 100 parts of methylaniline, 100 of potassium chlorate, and 150 of mercuric chloride. A similar result is obtained by substituting 300 parts of mercuric iodide for the 150 of chloride in the last recipe.

A new source of methylaniline and ethylaniline has been discovered by Spiller\* in the 'Hofmann gum,' a dark-coloured resinous substance produced in considerable quantity in the manufacture of Hofmann violet. This gum, when dried and submitted to destructive distillation, yields nearly pure methylaniline or ethylaniline, according as the 'gum' has been derived from methylic or ethylic iodide. The methylaniline from this source boils at  $392^{\circ}$  F., and does not yield crystalline compounds with acids. With arsenic acid it furnishes a reddish-violet dye, which may be converted into others of bluer shades by treatment with methyl iodide, as in the Hofmann process. The ethylaniline boils at about  $405^{\circ}$  F. Neither of these bases yields Girard's blue when heated with rosaniline.

A violet, called by the fanciful name of 'Dorothea violet,' and closely resembling a Hofmann violet, is produced by heating to  $212^{\circ}$  F., for two or three hours, a mixture of 100 parts of alcohol, 70 of rosaniline, and 14 of ethyl

---

\*Proc. Roy. Soc., xxi., 204.



nitrate. In this reaction ethyl nitrate is substituted for the more expensive ethyl iodide employed in the Hofmann process.

Various benzylic violet colours have been obtained by the action of benzyl chloride not only on rosaniline but also on the reddest shades of Hofmann and Paris violets, the tendency of the benzylation being to give the colour a bluer shade.

The *benzyl chloride* or  $\beta$ -chlorotoluene  $C_6H_5.CH_2Cl$ , required for this purpose, is prepared by the action of chlorine on boiling toluene, the hydrocarbon being distilled in a current of the gas. The condensed product is then rectified, and all that passes over below  $338^\circ F$  submitted to a fresh chlorination. In this manner an oil is obtained, which, when carefully fractioned between  $345^\circ$  and  $350^\circ F.$ , yields benzylic chloride equal to about 90 per cent. of the toluene originally employed.

Violet colouring matters have also been prepared from certain of the mixed tertiary monamines, such as methyl-diphenylamine, benzyldiphenylamine, benzylphenyltolylamine, and benzylditolylamine. A very fine violet blue is obtained from ethyldiphenylamine by heating at  $120^\circ F.$  to  $160^\circ F.$ , for four or five days, a mixture of 15 lbs. of the hydrochloride of the base, 5 lbs. of sulphate of copper, 1 of chlorate of potassium, 100 lbs. of pure siliceous sand, and 10 of the hydrochloride obtained by saturating oil of turpentine with hydrochloric acid. The mixture is placed in flat copper dishes in a stove, and frequently agitated. There should be a free circulation of air, which must be kept charged with moisture by means of a jet of steam. When the reaction is complete, the mass is washed with water to remove soluble salts, and the colouring matter extracted from the residue by means of alcohol or strong hydrochloric acid. In the former case, the alcohol is recovered by distillation; in the latter, the colouring

matter is precipitated by water saturated with common salt. It is purified by treatment with a caustic alkali, and after well washing with water, taking it up with acetic or hydrochloric acid.

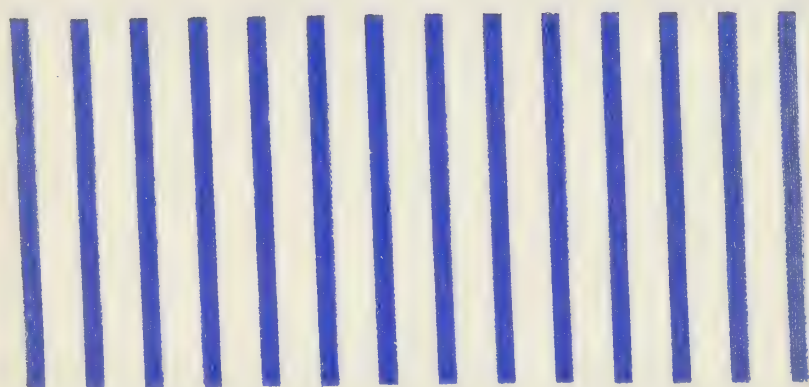
Mr. Wanklyn also proposed to treat rosaniline with isopropyl iodide obtained by the action of phosphorus and iodine on glycerin. The violet colour obtained was purified by a treatment similar to that employed for Hofmann violet, but its use was always restricted.

A very fine violet known as '*Britannia violet*' is obtained by a process devised by Mr. Perkin. He heats 6 parts of magenta, dissolved in 30 of methylated spirit, to 300° F., for eight hours with 4 parts of brominated oil of turpentine, a thick oily substance of the composition  $C_{10}H_{15}Br_3$  produced by the action of bromine on oil of turpentine in the presence of a large quantity of water. It possesses the golden-green iridescence common to the aniline colours, and can be manufactured of any shade from purple to a blue-violet.

An aldehyde violet was discovered in 1860 by Lauth, who prepared it by treating an alcoholic solution of magenta with a mineral acid, and then adding aldehyde. Various shades of violet, passing ultimately into blue, are produced according to the time the action is allowed to proceed. It is stopped at the proper point by neutralizing the acid with caustic soda, and, if necessary, precipitating with common salt. The dye is readily soluble in water, and dyes beautiful shades, but they are wanting in solidity.

The aniline purples are tested in the same manner as magenta; but it occasionally happens that the colour is not homogeneous, one portion being soluble in water, and another in alcohol. In dyeing, the same general principles are observed as when magenta is employed. Hofmann, Paris, and Britannia violets are soluble in water, but most of the others require to be dissolved in spirit, or what s

better, a mixture of alcohol and glycerin. For woollen goods with Hofmann or Paris violets they should be entered at 120° F., and the temperature very gradually raised to 212° F. The same processes are followed for cotton and mixed goods as with magenta.



HOFMANN VIOLET ON COTTON.

The following is Messrs. Lloyd Dale's process for fixing aniline colours on cotton :—500 or 600 grammes of pure tannin are dissolved in 9 litres of gum water, and an amount of aniline colour added sufficient to give the desired shade. After printing and steaming, the pieces are entered at 135° to 180° F. in a bath of tartar emetic, containing 13½ grammes of the salt per litre, then washed and dried. The pattern may also be printed on with a thickened solution of tannin, the strength of which varies with the shade required (20 grammes of tannin per litre for pale, and 130 for full shades), steamed, and passed through the bath of tartar emetic. They are then well washed and dyed in the bath of aniline colour, gradually raising the temperature to boiling, at which it is maintained for about twenty minutes. The pieces are finally washed and slightly soaped.



ANILINE BLUES.—A great variety of processes have been proposed for the preparation of aniline blues, but at the present time only a few of these are in actual use.

The '*Bleu de Paris*,' obtained by Messrs. Persoz, De Luynes, and Salvetat in 1861, is prepared by heating a mixture of 9 parts of stannic chloride and 16 of aniline to a temperature of 360° F., for thirty hours in a closed vessel. The black viscous mass is extracted with boiling water, and the colouring matter precipitated with common salt. Several re-solutions in water, and reprecipitations with salt are necessary to purify it. It may be obtained in the crystalline state by deposition from boiling alcohol. It is precipitated from its aqueous solution by acids, by alkalis, and by salts. Unfortunately the bleu de Paris is difficult to prepare in large quantities. Another blue, which is probably identical with this, is obtained by the process Delvaux. It merely consists in heating aniline hydrochloride, in closed vessels, to a temperature of 460° F.

The preparation of *Bleu de Mulhouse*, as carried out by Messrs. Gros Renaud and G. Schaeffer, is as follows: 250 grammes of rosaniline nitrate, 100 of white lac, and 36 of sodium carbonate are boiled for an hour, with 1 litre of alcohol and 3 of water.

M. Marnas, of the firm Guinon, Marnas, and Bonnet, Lyons, devised a process by which aniline is oxidised to a blue colour by means of peonine. The preparation of 'azuline,' as this blue is called, will be described when treating of the colours obtained from phenol.

*Bleu de Lyon*.—This colour, which is formed when magenta is heated with excess of aniline, was patented in January, 1861, by Messrs. Girard and De Laire. Although it is very largely manufactured, there are considerable difficulties in its preparation: in this it differs remarkably from magenta, which can be made in any quantity and of constant composition, for it requires not only properly

selected materials, but also skill and constant care on the part of the operator.

The aniline employed should be as pure and as free from toluidine as possible; that which distils over in the manufacture of magenta answering admirably for this purpose. The nature of the acid with which the rosaniline is in combination is also important, the best results being obtained with acetic, benzoic, valeric, and oleic acids. Practically it is not necessary to prepare these salts; a mixture of rosaniline hydrochloride and sodium acetate or benzoate being employed, which gives by double decomposition sodium chloride and rosaniline acetate or benzoate.

The operation is conducted in cast-iron pots capable of holding 3 to 5 gallons each, and furnished with a stirrer, the rod of which passes through a stuffing box in the lid. There are also two other openings in the lid; one closed by a wooden plug, through which a small sample of the contents may be withdrawn from time to time, to enable the workman to judge of the progress of the operation; the other is connected with a bent tube to condense any aniline that may pass over. These pots are heated to a uniform temperature of  $360^{\circ}$  F. by means of an oil bath: six pots being usually arranged in the same bath. In preparing the blue, a mixture of 30 lbs. of aniline and 10 lbs. of rosaniline acetate (or a corresponding quantity of a mixture of magenta, with dry sodium acetate or benzoate), is introduced into the pots, which are then heated in the oil bath. At first the red colour of the mixture changes slowly, but afterwards with rapidity: as soon as a sample taken out with a rod gives a pure blue colour when placed on a porcelain plate and moistened with a mixture of alcohol and acetic acid, the reaction may be considered as complete; to ascertain this point with precision, considerable experience is necessary. In a well managed operation the



blue should remain dissolved in the aniline, the whole forming a liquid of about the consistence of treacle.

In order to separate the large excess of aniline, the crude product may be washed with dilute acid, or the aniline may be mechanically removed by distilling it off in a current of steam; the former process is preferable, as it removes most of the red and purple impurities. This yields a cheap blue, fit for certain classes of dyeing; but in order to obtain pure tones, it is necessary to submit it to further processes of purification.

A much purer quality may be obtained by mixing the crude product with alcohol, and then pouring it into water acidulated with sulphuric or hydrochloric acid. The precipitate is collected and well washed with boiling, very dilute acid. 'Night Blue,' or 'Bleu Lumiere,' is merely a pure salt of triphenylrosaniline,  $C_{20}H_{16}(C_6H_5)_3N_3$ , which keeps its colour when seen by artificial light. It is prepared from the refined blue by washing it with cold alcohol, dissolving it in boiling alcohol, and then precipitating the free base by means of caustic soda. The base is collected, washed with boiling water, and then combined with the quantity of acid necessary to form a salt. The great inconvenience of this process is that it requires large quantities of alcohol. Several other processes have been proposed for the same purpose, the most recent consisting in the employment of aniline or a mixture of aniline and alcohol as a solvent.

By slightly varying the proportions of the materials and the circumstances of the experiment, blue of various shades can be obtained: of these there are four recognised in commerce, as B., B.B., B.B.B., and B.B.B.B. respectively.

The shade B. is made by heating to  $355^{\circ}$  F. a mixture of 2 kilos of pure rosaniline, 3 of pure aniline, and 270 of benzoic acid or glacial acetic acid. When the reaction is complete, the product is poured with constant agitation into



10 kilos of concentrated hydrochloric acid; the precipitate is collected, and washed by repeatedly boiling it with a large quantity of water. The precipitate, when collected, pressed, and dried, weighs  $3\frac{1}{2}$  kilos.

For the shade B.B. 5 kilos of aniline are used instead of 3, and when the reaction is complete the product is mixed with 7 or 8 kilos of alcohol and boiled. As soon as it is cool, the colour is precipitated by 10 kilos of concentrated hydrochloric acid, and then treated as for B. The yield is about 1300 grammes.

The shades B.B.B. and B.B.B.B. are obtained by purifying B.B. by dissolving it in alcohol, or a mixture of alcohol and aniline, adding alcoholic soda, filtering, and precipitating with hydrochloric acid.

The following process for preparing aniline blue and violet by the same operation is given by M. Bardy. Magenta is mixed with 30 per cent. of its weight of sodium acetate, and the whole evaporated to dryness; free aniline and crystallised potassium acetate are then added, equal to 10 per cent. of the rosaniline hydrochloride, and the mixture heated to  $347^{\circ}$  F. for several hours, until it acquires a pure blue colour. The product is then boiled for some time with one and a half times its weight of strong hydrochloric acid, which dissolves the purple colouring matters, whilst the insoluble blue floats on the surface, and may be removed. The blue is purified by washing it with water, and then boiling it with 5 times its weight of caustic soda solution at  $32^{\circ}$  B. for twenty minutes, diluting with 15 parts of boiling water, and filtering. The base is then freed from traces of the purple by washing with hot alcohol, and finally converted into sulphate by boiling it with its own weight of sulphuric acid, diluted with 10 parts of water. When the excess of acid has been removed by washing, it is fit for use. To extract the purple dyes from the concentrated hydrochloric acid solution, it is first dilu-

ted with water in the proportion of 9 parts for every 8 of the crude blue, this throws down diphenylrosaniline hydrochloride, a violet of a very blue shade, and on diluting the filtrate from this, with more water (about 180 parts) the monophenylrosaniline violet is precipitated.

The *Bleu de Paris*, previously described, has often been stated to be identical or nearly identical with the *Bleu de Lyon* or triphenylrosaniline. They are, however, widely different in their nature, the former being easily soluble in water and readily crystallising in sharply defined deep blue needles with a coppery reflection, whilst the latter cannot be obtained in distinct crystals, and it is insoluble in water. This circumstance forms a great drawback in its use, as when the alcoholic solution employed for dyeing is poured into the bath, the colour is precipitated in a finely divided state, and much of it only adheres mechanically to the goods, so that it afterwards rubs off. It may be kept in solution by the use of large quantities of alcohol, but this adds greatly to the cost of dyeing.

Mr. Nicholson, in 1862, discovered a process by which these blues might be rendered perfectly soluble in water; this consists in forming conjugate sulpho-acids with them, similar to the soluble compounds obtained by treating indigo with sulphuric acid. Of these acids four are known to exist, and have been carefully examined.\* They differ from triphenylrosaniline in having one, two, three, or four atoms of the hydrogen in the phenyl replaced by the group  $\text{HSO}_3$ ; the stronger the acid and the higher the temperature the greater the number of hydrogen atoms replaced. In the early attempts to prepare these soluble blues the higher sulphonic acids only were obtained, which had the disadvantage of giving shades which were less fast under the influence of light, soap, and alkali than the *Bleu de Lyon* itself. At present, however, a sodium salt of

---

\*Bulk : Deut. Chem. Ges. Ber., v., 417.



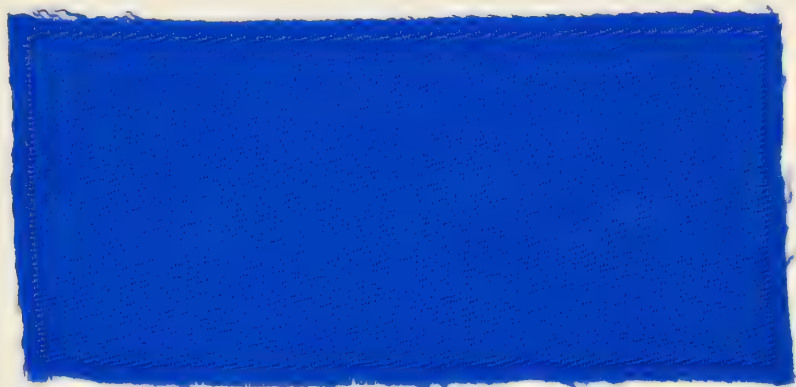
triphenylrosaniline-monosulphonic acid,  $C_{20}H_{16}(C_6H_5)_2(C_6H_4.SO_3Na)N_3$ , can be obtained, known as 'Nicholson's Blue,' which is fast, and well adapted for the use of the dyer.

Formerly a very large excess of sulphuric acid was employed in the manufacture, the proportion being 20 lbs. of aniline blue, and 80 of sulphuric acid, which were mixed and heated to a temperature of  $270^{\circ}$  F., until the mass had become homogeneous, and a sample, taken out for that purpose, dissolved completely in water when excess of ammonia was added. It was then poured into about 8 times its weight of water, and the precipitated blue, which is insoluble in the strongly acid liquid, collected and washed until the colour began to dissolve and pass through the filter. It was then pressed, and heated with a slight excess of ammonia in an enamelled cast-iron vessel until the coloured salt floated on the surface as a bronzy layer. It only required to be dried and ground, in order to be in a fit state for the market.

In the methods more recently adopted, a sulpho acid is produced which is insoluble in water; this is converted by treatment with an alkali into a salt soluble in water, which is then used in dyeing. The blue known as 'Nicholson's Blue' is a compound of this kind, being as before stated, nearly pure sodium triphenylrosaniline-monosulphonate. To prepare the monosulphonic acid: 1 kilo of refined blue is added, in small portions at a time, to 3 litres of sulphuric acid of density 1.76, and the mixture heated on the water bath until a sample poured into water gives a deep blue precipitate, which, after being washed until no longer acid, should not colour the water, but must be completely soluble in ammonia: this usually takes about five or six hours. The product is then poured into 30 litres of water with constant agitation, collected on woollen filters, and thoroughly washed. The pure acid thus obtained, is converted into the sodium salt by digesting it with a quantity



of soda-ley, not quite sufficient for saturation, filtering the solution, and evaporating in enamelled basins in a heated chamber. It then forms a grey-black amorphous mass, which dissolves easily in hot water. As met with in commerce it is frequently mixed with an excess of carbonate of soda.

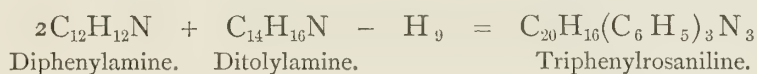


ANILINE BLUE ON WOOL.

A toluidine blue, very similar to the triphenylrosaniline salt known as the 'Bleu de Lyon,' may be obtained by heating rosaniline acetate with twice its weight of toluidine. Abundance of ammonia is evolved, and a brown mass with metallic lustre is obtained, which is soluble in alcohol with a deep indigo-blue colour. This dye is the acetate of tritolylosaniline, a base which may be regarded as rosaniline  $C_{20}H_{19}N_3$  in which three of the hydrogen are replaced by tolyl, and having the formula  $C_{20}H_{16}(C_7H_7)_3N_3$ .

*Diphenylamine blue.*—Hofmann was the first to notice that a blue colour was produced by the action of various reagents on diphenylamine; the discovery of a diphenylamine blue fit for use in dyeing is due, however, to Messrs. Girard and De Laire. It is prepared in a manner similar to magenta, by the action of oxidising agents on a mixture

of diphenylamine and ditolylamine, and is in all probability identical with the Bleu de Lyon. Its formation would then be represented by the equation:—



When three equivalents of aniline are heated to about 460° or 470° F. with two of aniline hydrochloride in a flask furnished with a condensing tube, a reaction takes place, accompanied by disengagement of ammonia and formation of diphenylamine. The operation, however, is very tedious, only about one-eighth of the aniline being converted after 30 hours' digestion. In order to extract the diphenylamine, the product is dissolved in hydrochloric acid and diluted with a large quantity of hot water; this decomposes the diphenylamine hydrochloride, and the liberated base floats on the surface in the melted state. It may be purified by recrystallisation from ether or benzene.

In order to prepare the commercial diphenylamine, which, as has previously been stated, is a mixture of diphenylamine and ditolylamine, a suitable aniline is chosen and a portion converted into hydrochloride; 740 lbs. of this hydrochloride and 100 of the aniline are introduced into an enamelled cast-iron vessel, closed by a lid and furnished with a safety valve, a manometer, a screw valve opening into a tube connected with a worm, and a tube closed at the lower end and long enough to dip into the mixture in the boiler; this tube is partly filled with mercury, into which is plunged the bulb of a thermometer. The mixture is gradually heated, and kept for about two hours at a temperature of 420° to 428° F.; the screw valve is now closed, and the temperature gradually raised to about 480° F., during which the pressure in the interior increases to about 5 atmospheres. The time required for an operation is 12 hours, during the last 6 of which the temperature should be 465°—500° F. When cold, the product is

removed from the boiler, dissolved in 140 lbs. of hydrochloric acid by the aid of a gentle heat, and poured into 60 or 80 gallons of water; this precipitates the diphenylamine, whilst the unaltered aniline remains in solution as hydrochloride. The diphenylamine, after being washed first with water and then with a dilute alkaline solution, is purified by distillation, or by crystallisation from coal oil or petroleum.

Although almost all the oxidising agents which have been proposed for the preparation of magenta may be employed to transform diphenylamine into the blue colouring matter, trichloride of carbon  $C_2Cl_6$ , is that which has been found to give the best results. The operation is conducted in enamelled iron retorts of the capacity of about 10 gallons, furnished with agitators, and heated in an oil bath. A mixture of 24 lbs. of carbon trichloride, and 20 lbs. of the diphenylamine are introduced into each of these, and the temperature gradually raised to  $355^{\circ}$  F. which should not be exceeded, as otherwise a portion of the blue is apt to be destroyed. During the reaction carbon dichloride (perchlorethylene),  $C_2Cl_4$ , distils, the quantity of which corresponds very nearly to that of the trichloride originally employed. When the operation is finished, which usually occupies three or four hours, and the product is cold, it is dissolved in twice its weight of aniline heated to  $212^{\circ}$  F. This solution is then poured very slowly into ten times its weight of coal oil with constant agitation; the blue is precipitated by this means as an impalpable powder, which is collected, washed with coal oil, and again dissolved and reprecipitated in a similar manner. Finally, it is redissolved in twice its weight of aniline, precipitated by 4 parts of hydrochloric acid, collected, and washed with boiling water. The crude blue may also be purified by boiling it with soda solution, extracting the resinous matters from the pulverised base

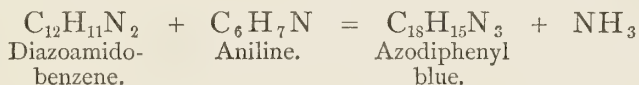


by hot petroleum, dissolving the residue in alcohol, and precipitating by hydrochloric acid.

Another process, devised by Brimmeyr, consists in heating the diphenylamine to about  $245^{\circ}$  F. for four or five hours, with an equal weight of oxalic acid; the amount of colouring matter produced is but small, however.

This blue, which is insoluble in water, gives very pure shades in dyeing.

*Azodiphenyl blue.*—This blue is prepared by heating 1 part of azodiphenyldiamine (diazoamidobenzene, p. 429), 1 part of aniline, and 2 of alcohol to  $320^{\circ}$  F. for four or five hours. The dark blue product is then washed with boiling water, dissolved in a mixture of alcohol and hydrochloric acid, and the base thrown down with caustic soda. By dissolving the well washed base in a mixture of hot alcohol and hydrochloric acid, and concentrating the solution if necessary, a dark blue crystalline hydrochloride is obtained, which is insoluble in water, but readily soluble in alcohol, especially if it is warm. The composition of the hydrochloride is  $C_{18}H_{15}N_3.HCl$  the base being formed in the manner represented in the following equation:—



This blue has the same composition as violaniline, but nothing is known at present of the relation between the two substances.

This colour dyes wool and silk of a deep violet-blue.

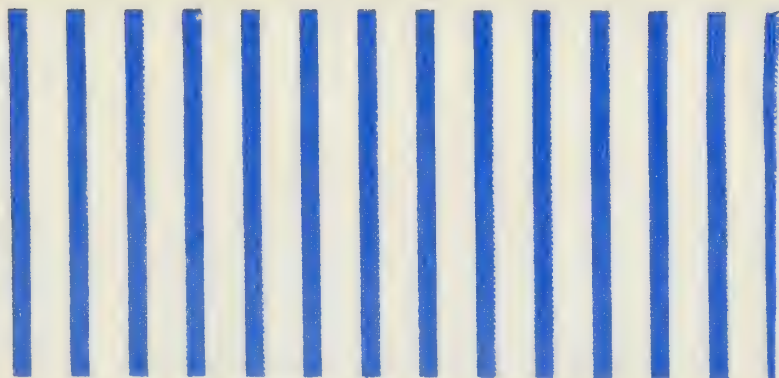
A variety of processes are employed in dyeing with aniline blues. Those which are insoluble in water, are dissolved in alcohol and wood spirit, or a mixture of these with glycerin; the purer the blue, the more solvent does it require. Like most of the aniline colours, they dye wool and silk without mordants; a hot bath acidulated with sulphuric acid, being used for the former, and one of a lower temperature, acidulated with tartaric acid, for the latter.

The soluble sodium salt of the monosulphonic acid of triphenylrosaniline (Nicholson Blue), only gives feebly coloured solutions, but the colour comes out with great intensity when a mineral acid is added to them. Woollen piece goods are usually entered into the bath rendered alkaline with soda, water glass (an alkaline silicate), or borax, at 120° F., and the temperature gradually raised to near the boiling point, at which it is kept for about half an hour. The wool extracts the salts in the colourless state, and has such an affinity for them that they cannot be removed by washing with water: on dipping them in an acid, however, the base is removed, and the coloured acid remains combined with the fibre. In order to watch the progress of the dyeing, several strips of the same stuff are attached to the pieces, one of which is removed from time to time, washed, and dipped in acidulated water to bring out the colour. When the required shade has been attained the pieces are taken out, winced in cold water, and then passed through a bath of dilute sulphuric acid to develop the colour: they are finally thoroughly washed in cold water.

A blue of this class, manufactured by Messrs. Brooke, Simpson, and Spiller, is a very permanent colour, and is sometimes used with camwood to produce a cheap imitation of an indigo vat blue.

The soluble blue consisting of the higher sulpho-acids, which now comes but little into the market, dyes silk and wool with moderate facility if the bath is acid, but not if it is neutral or alkaline.

The aniline blues have no affinity for cotton fibre, and the attempts to dye them with various mordants have not been very successful. Cotton skeins may, however, be died blue by working them first in a solution of alum and then in soap: the fibre thus mordanted takes up the blue readily, but although it resists light fairly, it cannot be washed with soap.



## NICHOLSON'S BLUE ON COTTON.

In printing, the same processes with albumen and lactarin may be employed for the blue, as those previously described for magenta. Perkin's arsenious acid process, slightly modified, can also be used. The thickened aniline colour is mixed, according to its strength, with one-eighth to one-fourth of its bulk of a saturated solution of arsenious acid in glycerin, and an equivalent quantity of acetate of alumina. The mixture is then printed and steamed for forty-five minutes, after which it is worked in boiling soap-lye for half an hour to brighten the colour.



## CHAPTER XIV.

### ANILINE GREEN.—ANILINE YELLOW.

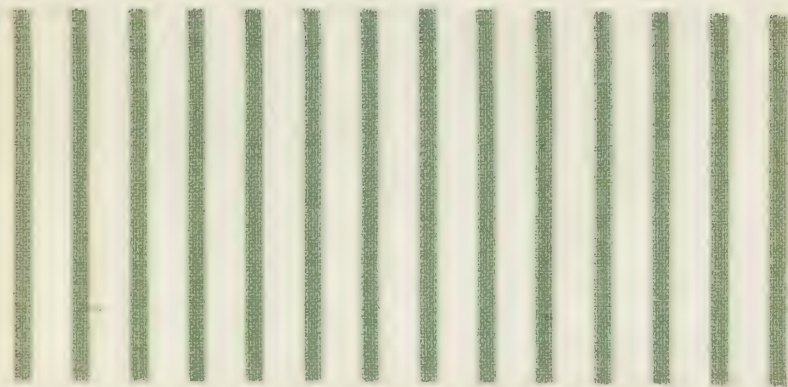
ANILINE GREENS.—One of the first of these colours obtained from aniline was a deep green, called 'emeraldine,' for which Messrs. Calvert, Clift, and Lowe took out a patent in 1860. The fabric was first prepared by passing it through a bath containing one part of potassium chlorate in 200 of water; it was then dried, and printed with an acid aniline hydrochloride. After ageing for a few hours the colour is developed, and the goods only require to be well washed. When passed through a solution of potassium bichromate, the colour is changed to a deep indigo-blue, which was called 'azurine.' Both these colours are dull.

*Aldehyde green*, a very beautiful colour, was accidentally discovered in a remarkable manner. In 1861 Lauth had succeeded in obtaining a blue dye by the action of aldehyde on an acid solution of aniline; there was, however, great difficulty in fixing it. Shortly afterwards Cherpín, the chemist to the dyeworks of M. Usèbe, near St. Ouen, tried several experiments with the colour, during which he mentioned to a photographic friend the difficulty there was in fixing the colour; this gentleman naturally suggested hyposulphite of sodium, with which he was in the habit of 'fixing' his photographs. On making the apparently useless experiment, M. Cherpín found that the blue was converted into a splendid green dye, now known as 'aldehyde green.'

In 1862 a patent was taken out for the production of this colour in the following manner:—2 lbs. of rosaniline

are dissolved in 4 lbs. of sulphuric acid of density 1.63 which has previously been diluted with 1 lb. of water. When complete solution has been effected, 8 lbs. of a strong alcoholic solution of aldehyde is added in small portions at a time, and the mixture gently heated until a drop of it, when allowed to fall into water, gives a fine blue coloration without any shade of red. As soon as the reaction is complete, which ordinarily takes place in about 20 minutes, the product is poured into a boiling solution of 8 lbs. of sodium hyposulphite in 5 gallons of water. The mixture is then boiled for 7 or 8 minutes, and the beautiful green-coloured solution separated by filtration from the bluish-grey insoluble precipitate.

The green solution may be precipitated by acetate of sodium, tannin, or oxide of zinc, and the green paste dried, or employed for dyeing in the moist state. This green is employed chiefly in silk dyeing, and gives splendid shades, which are very brilliant, both by artificial light and by daylight; as, however, it cannot be kept any length of time without deterioration, dyers usually prepare it for themselves as they require it.



ALDEHYDE GREEN ON COTTON.

The composition and chemical nature of this substance have not as yet been accurately determined; it is undoubtedly the salt of an organic base, to which Hofmann assigns the formula  $C_{22}H_{27}N_3S_2O$  and which may be obtained by decomposing an aqueous or alcoholic solution of aldehyde green with soda or ammonia. It is of a pale green colour, and slightly soluble in alcohol. With acids it forms bright green salts, which are very unstable.

According to Lauth, this green is produced whenever aldehyde blue is brought in contact with nascent sulphur, an hypothesis which is strongly supported not only by Hofmann's analysis of the base, but also by Hirzel's method of preparation, in which the aldehyde blue is treated with ammonium sulphide, in place of the hyposulphite. Lucius maintains, however, that aldehyde green exists ready formed in the solution obtained by the action of aldehyde on an acid solution of rosaniline, and that the sodium hyposulphite merely removes the blue and violet-coloured substances produced at the same time.

*Iodine green.*—By far the most important of the aniline greens is that known as the 'iodine green,' which is always produced in larger or smaller quantity, when an excess of methyl or ethyl iodide acts on an alcoholic solution of rosaniline, Hofmann violet being first produced, which is then converted, by the continued action of the iodide, into *dimethyliodide of trimethylrosaniline*  $C_{20}H_{16}(CH_3)_3N_3(CH_3I)_2$  if the methyl compound has been employed. An explanation of the fact that this green colouring matter was not observed until two years after the discovery of the Hofmann violet, and during which such enormous quantities of the latter were manufactured, is offered by the circumstance that the most favourable conditions for the production of the violet are those which are most unfavourable for the formation of the green. It was only, therefore, when the ordinary methods were departed from, that the green was



produced in quantity sufficient to be isolated, and its properties ascertained.

On this account it is somewhat difficult to fix the exact date of its discovery. Messrs. Tillmanns de Crefeld, Meister, Lucius, Brüning, Poirrier, and Chappat all seem to have manufactured it in 1865. To Mr. Wanklyn, however, is due the merit of first having published a process for its preparation. This was contained in a patent dated the 6th of November, 1865; and although itself of comparatively little value from an industrial point of view, it has served as the starting point for the present successful methods.

Wanklyn's process consisted in heating equal parts of rosaniline, methyl iodide, and methyl alcohol for three hours to 230° F.; the product, which is principally Hofmann violet, is washed with a dilute solution of sodium carbonate, decomposed by caustic soda, and the liberated base, after being dried and pulverised, is again treated with the alcoholic iodide; a third operation suffices to convert nearly all the violet into green. As the latter is very soluble in dilute solutions of sodium carbonate, it is easily separated from the violet which has not been converted, and also from the impurities produced at the same time.

Important improvements have been made in this manufacture by Hofmann and Girard; for although all the salts of rosaniline are capable of being converted into the green, yet some give much better results than others, such as the sulphate, nitrate, benzoate, and especially the acetate. As the presence of water interferes considerably with the reaction, it is advisable that all the materials should be in as dry a state as possible; moreover, as the iodine green begins to decompose at 230° F., care must be taken that the temperature should never exceed that point.

The iodine green is now manufactured in enamelled  
CC

iron digestors of a capacity of about 16 or 20 gallons, and capable of bearing an internal pressure of twenty to twenty-five atmospheres. The lid is furnished with a pressure gauge, and also with a screw tap communicating with a worm, so that at any given moment the liquid products of the reaction may be allowed to pass off, and be condensed. The apparatus is heated by means of a water bath or a double steam jacket, care being taken that the temperature never rises above 230° F. Twenty lbs. of pure dry rosaniline acetate, 40 of pure methyl iodide, and 40 of highly rectified methylic alcohol, boiling at 147°—152° F. are introduced into the apparatus, which is gradually heated. The pressure in the interior of the digester, as indicated by the manometer, rapidly increases to eight atmospheres, and then more slowly to ten or eleven, which it never ought to exceed. In the course of four or five hours, when the reaction is complete, the steam is shut off, and the apparatus is allowed to cool. The pressure then gradually falls to about four atmospheres, when the screw valve is opened, and the volatile products removed by distillation. Besides the methylic alcohol and excess of methyl iodide, there are considerable quantities of methyl acetate and oxide formed, the latter of which escapes with violence on opening the valve. The semi-fluid mass containing the colouring matters is poured into a large vat, heated by steam, and containing 120 gallons of hot distilled water: here the green dissolves entirely, together with a small portion of the violet, which is kept in solution by the acid set free during the reaction; the greater portion of the violet, however, remains undissolved, and is separated by filtration. To the clear filtered liquor, which must be kept boiling, 70 lbs. of common salt are added, and the free acid is then carefully neutralised with crystallised sodium carbonate in order to precipitate the violet still in solution. To ascertain the exact point when all the violet



has been thrown down, a sample is withdrawn from time to time, filtered through sand, and a skein of silk immersed in the hot liquid. When the silk becomes dyed a pure green colour without any admixture of violet, it is a sign that sufficient sodium carbonate has been added; the amount usually required for this purpose being rather more than 3 lbs. After the solution has become quite cold, it is filtered through a sand filter to remove the finely divided violet, and then precipitated with a cold saturated aqueous solution containing about 6 lbs. 14 ozs. of perfectly pure picric acid. In this way a picrate of the iodine green is obtained, which is only very slightly soluble in water; as it is in a fine state of division, it is collected, washed slightly, and allowed to drain until it becomes of a pasty consistence, in which form it is sent into the market. Although it possesses great tinctorial powers, its solubility in water is so slight that it is necessary to employ it in alcoholic solution.

In a well conducted operation about 60 per cent. of the colouring matter obtained is green, and about 40 violet. The latter may be converted into green by further treatment with methyl iodide in the following manner:—The precipitated violet iodide, after having been carefully washed and dried, is finely powdered, and dissolved in alcohol, adding sufficient caustic soda in alcoholic solution to combine with the hydriodic acid and liberate the base. The whole is now introduced into a vessel furnished with an agitator and a return condenser, and the requisite quantity of methyl iodide added. The liquid is carefully heated by means of a water bath, to the temperature of 120° F., and as the production of the green is very rapid, care must be taken to stop the action as soon as the transformation is complete, by cooling rapidly, adding acetic acid, and pouring into a large quantity of hot water. After the removal of the unattacked violet by means of common salt and



carbonate of soda, the green may be precipitated by picric acid as before. This green is generally purer than that made directly from rosaniline, and gives finer shades in dyeing.



WOOL DYED WITH IODINE GREEN.

*Soluble green.*—The inconvenience arising from the insolubility of the picrate in water has led to the substitution of a salt of zinc, such as the acetate, chloride, or sulphate, for picric acid in the precipitation of the green from its aqueous solutions containing common salt. The precipitates, which are soluble in water, are double salts of zinc and iodine green, and may be prepared either from the product obtained directly from rosaniline, or that from Hofmann violet; in the latter case the colour is purer. The shade which the zinc compound gives in dyeing is less yellow than that of the picrate.

*Crystallised green.*—The iodine green may be obtained in a crystalline state from a concentrated solution. For this purpose, the crude product from 20 lbs. of rosaniline is poured into 24 gallons of boiling water, and after separating the precipitated violet and adding 14 lbs. of common salt, the violet in solution is *completely* removed by adding a slight excess of sodium carbonate, even at the risk of

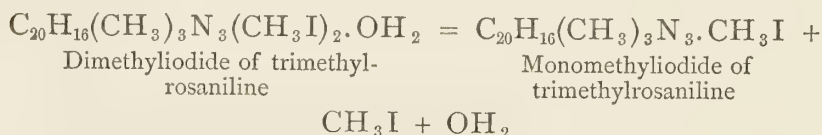
destroying a small quantity of the green, which is easily altered by ebullition with the alkaline salt. The solution, which should be filtered boiling hot into vats containing copper rods, deposits the dye in beautiful green needles with a metallic-bronze lustre. The finest are formed on the rods and sides of the vessel, whilst at the bottom there is a crystalline crust, which is less pure. It is fit for use after being washed once or twice with a small quantity of cold water to remove the adhering sodium chloride. In order to obtain it chemically pure, however, the purest green crystals should be dissolved in boiling absolute alcohol, the solution filtered, and then mixed with an excess of anhydrous ether; the crystalline precipitate thus produced, when again dissolved in boiling alcohol and allowed to cool slowly, deposits the pure salt in magnificent green prisms having a lustre equal to that of the elytra or wing cases of cantharides.

Iodine green, or *Dimethyliodide of trimethylrosaniline*, which in the crystalline state has the formula  $C_{20}H_{16}(CH_3)_3 N_3(CH_3I)_2 + OH_2$  is soluble in alcohol and in water, but insoluble in ether and in benzene. The corresponding acetate crystallises in slender needles, and the nitrate in prisms. Concentrated mineral acids, reducing agents, and oxidising agents, all destroy the green. When treated with alkalis, the iodine green is converted into the corresponding base, which is colourless: it may also be obtained from the picrate by decomposing its solution in ammoniacal alcohol with caustic soda.

*Transformation of iodine green.*—The crystals of iodine green become changed when left for some time in a vacuum, or when exposed to light; they will now be found to be only partly soluble when treated with water, yielding a green solution, and leaving a residue of a beautiful violet colour, which is extremely soluble in alcohol. This decomposition takes place in the course of a few hours at



212° F., and instantly at 300° F.; thus the green dissolves in boiling aniline with a splendid violet colour. In this case the green loses a molecule of methyl iodide and a molecule of water, and becomes transformed into *monomethyliodide of trimethylrosaniline* in the following manner:—



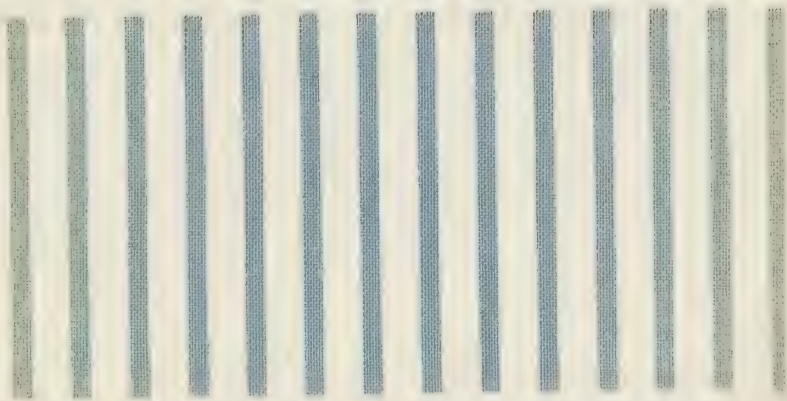
If a solution of iodine green in methyl alcohol be heated to 212° F. for two or three hours in sealed tubes, it splits up into monomethyliodide and trimethyliodide of trimethylrosaniline, the latter of which, being comparatively insoluble, separates as the liquid cools in long cantharides-green needles. It may also be obtained by the direct union of methyl iodide with aniline green. It is but very slightly soluble in boiling alcohol, giving a violet-blue solution.

*Perkin's green.*—There is also another green dye, a derivative of magenta, known in commerce by the above name. The method employed in its preparation has not been made public, but although it resembles the iodine green more closely than the aldehyde green, it differs from it in its solubility, and in being precipitated from its solutions by the alkaline carbonates such as sodium carbonate. It is also precipitated by picric acid, forming a picrate closely resembling that from iodine green, and which crystallises from alcohol in small prisms having a golden iridescence. This colour is now extensively employed, chiefly for calico printing.

*Methyl green.*—Dyes very similar to those prepared by the action of methyl iodide on magenta, may be obtained directly from methylaniline, or rather a mixture of methylaniline and methyltoluidine. When such a mixture is oxidised, it yields the so-called 'methyl violet,' or Paris



violet (p. 397), which appears to differ from Hofmann violet in retaining its colour when seen by artificial light. If this be methylated by treatment with methyl chloride, or methyl nitrate, 'methyl green' is produced. It may be separated from the unaltered violet by mixing the solution with chloride of zinc, and then gradually adding carbonate of soda. When the violet lake which is at first thrown down ceases to appear on the further addition of carbonate of soda, the solution is concentrated by evaporation, and on cooling, deposits crystals of a double salt of the methyl green hydrochloride, with chloride of zinc. It seems to differ from the iodine green in being more soluble in water, and in not being decomposed when its solution is boiled. It gives very fresh colours, and wool may be dyed with it without any preparation.



METHYLANILINE GREEN ON CALICO.

The violets obtained from the tertiary monamines, noticed on p. 399, also yield greens when properly treated with methyl iodide or nitrate.

The general principles of the methods to be used in dyeing with these greens are the same as those for the other aniline colours. In order to obtain full shades on wool, Dale recommends that it should be worked in a very dilute

solution of calcium hypochlorite (chloride of lime) before dyeing: it then takes up the colour very readily. In using the greens sold as insoluble tannates, they must be dissolved in water acidulated with sulphuric acid; wools and silk can then be readily dyed with them, employing the bath at a higher temperature for the former than for the latter.

The so-called 'Pomona paste' of commerce, does not require the use of alcohol, as it is readily soluble in water. Wool is dyed with it in the following manner. A bath is prepared having enough silicate of potash dissolved in it to give the water a soapy feel. In this the wool or woollen yarn is worked at a temperature of 160° F. until it is thoroughly wetted. The colour, which has previously been dissolved in a small quantity of cold water, is now added very gradually to the bath, and the wool worked in it until it has taken up the proper amount of colour. This is ascertained by taking out some waste scraps which have been dyed along with it, and dipping them into very dilute acetic acid. As soon as the proper shade is attained, the wool is taken out and put into a bath of very dilute acetic acid at 160° F., to which a little tannin, or extract of galls may be added to fix the colour. If a yellow shade of green is required, picric acid may be added to the bath.

To dye alpaca with aniline green, the thoroughly wetted stuff is worked in a bath containing 4 ozs. of aniline green, 4 ozs. of strong ammonia, and 4 ozs. of silicate of soda to each 10 lbs. of the material, then passed through a tannin bath, and again returned to the colour bath; finally, it is brightened in a somewhat strong acetic acid bath.

To dye cotton, it is first worked thoroughly in a tannin bath made with sumach, galls, or myrobalans, then in double muriate of tin. After this it is winced in water, and the cotton, thus mordanted, worked in a cold bath of the aniline green.



Linen may be dyed with aniline green after having been mordanted with tannin and acetate of alumina. The yarn is soaked for 12 hours in a tannin bath made by boiling 8 lbs. of sumach in water, after which it is mordanted with acetate of alumina made by adding a solution of 1 lb. of alum to one of  $1\frac{1}{2}$  lbs. of acetate of lead. The yarn thus prepared is worked in the bath of iodine green until it has acquired the proper shade. If a yellow tint is desired, the goods may be topped with picric acid.

Sevez recommends for printing, 1 litre of gum water, 250 grammes of paste green, and 150 grammes of bisulphite of soda. The mixture is heated in the water bath until homogeneous, and then allowed to stand for three or four days, when it is ready for printing. The colour will bear steaming, and yields more satisfactory results upon silk and worsted than upon calico.

ANILINE YELLOWS.—Generally speaking, the aniline yellow and orange colouring matters differ from those previously described, inasmuch as they are not regularly manufactured, but arise as bye products in the preparation of other aniline colours.

*Chrysaniline*, or *phosphine*, is a bye product obtained in the preparation of magenta, and which, according to Hofmann, has the formula  $C_{20}H_{17}N_3$  differing from that of rosaniline,  $C_{20}H_{19}N_3$ , by two atoms of hydrogen. It was first obtained by Nicholson from the magenta residues, by submitting them to a current of steam for some time, and then precipitating the chrysaniline by adding nitric acid to the solution. It is manufactured by Messrs. Brooke, Simpson, and Spiller, but their process is kept secret.

There is also a yellow compound formed by the action of oxidising agents on toluidine, discovered by Girard and Chapoteaut in 1866, which possesses characters almost, if not quite, the same as those assigned to chrysaniline. From the results of the analysis, and the mode of



formation, the substance *chrysotoluidine* is found to be a homologue of rosaniline, having the formula  $C_{21}H_{21}N_3$ . As there is but a very slight difference in the centesimal composition assigned to chrysaniline and chrysotoluidine respectively, it is possible that these two substances may be isomeric, if not identical. In fact, whilst chrysotoluidine has been prepared from crystallised toluidine, chrysaniline has been obtained from the residues of magenta made from commercial aniline, which is always rich in the isomeric liquid toluidine.

As already noticed, chrysotoluidine occurs along with violaniline and mauvaniline in the insoluble residue obtained in the manufacture of magenta, and a process has been given (p. 392) for isolating the mauvaniline. Girard and De Laire treat the crude magenta, obtained from the action of arsenic acid on aniline, in the following way:—2000 lbs. of the raw product are dissolved in 170 lbs. of hydrochloric acid diluted with 2500 gallons of boiling water. The violaniline remains undissolved, and is separated by filtration; 250 lbs. of hydrochloric acid are added to the filtrate, which, on cooling, deposits 80 or 90 lbs. of mauvaniline hydrochloride mixed with a little rosaniline and resinous matters; 1250 lbs. of common salt are added to the filtrate, which precipitates 60 to 70 lbs. of a mixture of mauvaniline and rosaniline salts, and after this has been separated 166 lbs. of soda ash (containing 60 per cent. of soda) is added. The precipitate thus obtained, which weighs 410 to 420 lbs., consists almost entirely of rosaniline salts, mixed, however, with a very small quantity of salts of chrysotoluidine.

After this has been separated, the filtrate is completely saturated by adding to it 75 lbs. more of soda ash; this throws down the chrysotoluidine as an amorphous precipitate weighing from 75 to 80 lbs. In order to purify it, 100 lbs. are boiled with 250 gallons of lime water

nitric acid to a solution of the monacid salt. It is decomposed by water, losing its acid, and being converted into the monacid salt.



## ANILINE YELLOW.

By treating chrysotoluidine with methyl iodide, three atoms of its hydrogen are replaced by methyl, giving rise to the iodide of a new base, *trimethylchrysotoluidine*,  $C_{21}H_{18}(CH_3)_3N_3$ , which crystallises in brilliant crimson needles. They are soluble in water, and dye wool and silk a brilliant orange-red.

Scheurer-Kestner obtained an orange dye by dissolving mauveine in dilute hydrochloric acid, and treating it with tin. When the metal has dissolved, and the solution lost its purple colour, the addition of common salt throws down a yellow precipitate, which is collected, pressed, and the colouring matter extracted by alcohol. It dyes silk and wool of a yellowish-orange colour, but it easily oxidises and becomes red.

*Diazoamidobenzene* and *amidodiphenylimide*,  $C_{12}H_{11}N_3$ , are isomeric compounds obtained by the action of nitrous acid on an alcoholic solution of aniline, the former at ordinary and the latter at higher temperatures. *Diazoamidobenzene*, or *azodiphenyldiamine*, crystallises in golden-yellow shining

and pressed, is converted into sulphate by the addition of the exact amount of sulphuric acid.

Chrysotoluidine may be prepared directly from the crystalline toluidine by the action of heat on the arseniate, but as that salt is difficultly fusible, it is advisable to add an excess of toluidine acetate. It then begins to fuse at  $265^{\circ}$  F., and at  $300^{\circ}$  F. decomposes, water being given off and an orange-coloured matter formed. Carbon trichloride or stannic chloride (bichloride of tin), may be conveniently substituted for the arsenic acid. The action is then perfectly regular, although a small quantity of ditolylamine is always produced.

In order to purify the crude product, it is boiled with excess of soda, the unaltered toluidine being driven off by a current of steam. The liberated base is then washed, dissolved in a slight excess of dilute hydrochloric acid, and precipitated by picric acid in excess. The acid picrate of chrysotoluidine thus obtained may be purified by crystallisation, and the base set free by treatment with a solution of caustic soda. Chrysotoluidine, may also readily be obtained by the action of nitrate of mercury on toluidine acetate.

Pure *chrysotoluidine*,  $C_{21}H_{21}N_3$ , is a yellow amorphous powder, resembling recently precipitated lead chromate. It is but slightly soluble even in boiling water, but is readily soluble in alcohol, ether, and benzene. When submitted to dry distillation, it yields ditolylamine. It unites with acids forming two series of salts, one monacid, and the other diacid. These, as a rule, crystallise well, the most remarkable being the nitrates. The nitrates form ruby-red needles, and are very insoluble, so that if a dilute solution of potassium nitrate be added to a moderately concentrated solution of a chrysotoluidine salt, a crystalline precipitate of the mononitrate is immediately produced. The diacid salt is formed on adding concentrated



It is sparingly soluble in boiling water, readily soluble in alcohol.

Jacobsen obtains a yellow colouring matter by the action of 4 parts of mercurous nitrate on 10 of aniline hydrochloride dissolved in 40 of water. After 24 hours the precipitate is redissolved in boiling water, which, on cooling, deposits it in a state of purity.

*Adulterations.*—The colours which come into the market as aniline yellow and aniline orange are mostly mixtures of yellow and red colouring matters. Naphthalene yellow and nitrophenol are often sold as aniline yellow, and will be found on examination to consist principally of picric acid or naphthalene yellow. Many of these mixtures may be detected by microscopical examination, or by treating the sample with cold water. The chief adulterant is picric acid, which may be readily recognised by its yielding the purple isopurpuric acid when treated with potassium cyanide, and when treated with chloride of lime, chloro-picrin, which makes itself known by its characteristic pungent odour. Chrysaniline generally contains arsenic, in some cases to the extent of 5 per cent. or more. The presence of picric acid is a decided evil, as it not only diminishes the brilliancy of the yellow colour, but acts prejudicially in other ways.

laminæ, which are sparingly soluble in cold alcohol, and insoluble in water. The isomeric amidodiphenylimide is a yellow crystalline powder which is identical with the product which Schiff\* obtained by heating to  $212^{\circ}$  F. 1 part of aniline nitrate dissolved in 10 of water, with 3 of sodium stannate. A reaction takes place, which may be considered to be complete when a sample of the liquid turns red on the addition of an acid. It is then allowed to cool, the stannic oxide removed by hydrochloric acid, and the residue purified by repeated solution in dilute boiling hydrochloric acid, and precipitation with ammonia. Its solutions, when slightly acidulated, dye silk and wool a deep lemon-yellow colour. The picrate gives a red shade. It yields a blue dye when heated with aniline.

It is a curious circumstance that both these isomeric aniline yellows are volatile, and may be removed from the dyed fabrics by the mere application of heat. This necessarily interferes considerably with their application in dyeing.

*Zinaline* is the name given by Vogel to a yellow dye obtained by the action of nitrous acid on solutions of rosaniline. It is slightly soluble in boiling water, moderately soluble in hot alcohol, and dyes wool and silk a pale orange, which is changed to red by ammonia. It dissolves in concentrated acids with a yellow colour, and with alkalis it gives a bright red solution, from which acids precipitate the zinaline unchanged. This substance, to which Vogel assigns the formula  $C_{20}H_{19}N_2O_3$ , melts below  $212^{\circ}$  F., and at a higher temperature gives off abundant yellow vapours, and then takes fire with slight detonation.

A substance which dyes silk and wool of a beautiful golden-yellow colour is also obtained from the mother liquors of magenta made by the nitrate of mercury process, after the red has been precipitated by common salt.

---

\*Compt. Rend., lvi., 1234.

prepared by submitting dinitrobenzene to the action of tin and hydrochloric acid.

Jacobson prepares browns by the action of oxidising agents on rosaniline. One process consists in heating aniline formate to  $212^{\circ}$  F. with a strong solution of ammonium chromate; in the other, picric acid is heated in a capacious vessel with two parts of commercial aniline. At first the picric acid dissolves, forming an orange-yellow oily liquid, but as the temperature rises it becomes brown, and at  $230^{\circ}$  to  $240^{\circ}$  F. evolves abundance of vapours. It should be kept at  $280^{\circ}$  to  $300^{\circ}$  F. until ammoniacal vapours cease to be given off, and a small portion thrown into water communicates but a faint yellow colour to the liquid; this usually takes some hours. The black mass is then poured with constant stirring into dilute hydrochloric acid, and in order to remove all the unaltered aniline and also a red colouring matter which is present, it is ground up and boiled repeatedly with successive portions of very dilute acid. It is finally collected, and washed first with an alkaline solution, and then with pure water.

This dye is insoluble in water, but if too high a temperature has not been employed in its preparation, it is completely soluble in alcohol. Its alcoholic solution is acidulated with sulphuric acid and mixed with glycerin, before it is added to the bath.

The crude colour may also be purified by dissolving it in concentrated sulphuric acid, pouring the solution into water, and precipitating with common salt. As thus prepared it is somewhat more readily soluble in alcohol.

This colour dyes silk a Corinth red, and wool a deep brown with a violet reflection.

M. H. Koechlin employs the brown colouring matter noticed by Hofmann when studying the action of oxidising agents on rosaniline. These colours may be fixed on wool by printing a mixture of gum water with 2 parts of oxalic



## CHAPTER XV.

### ANILINE BROWN.—ANILINE BLACK.

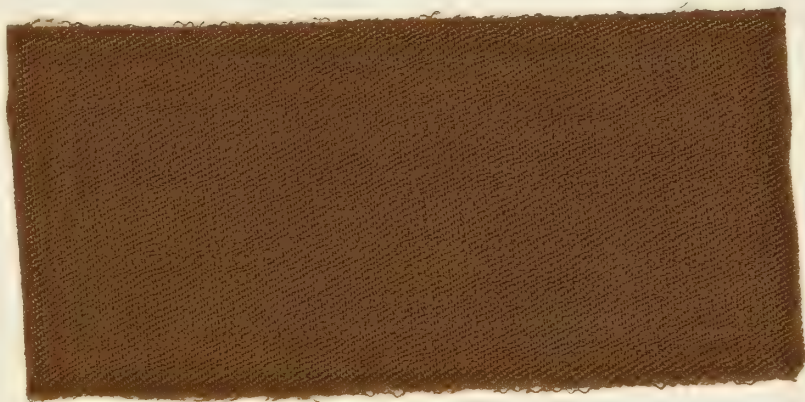
ANILINE MAROONS AND BROWNS.—These colours are only of secondary importance in dyeing. One of the first patents taken out for them was that of Messrs. Girard and De Laire for the production of a maroon. To 4 parts of dry aniline hydrochloride in a state of fusion, 1 part of dry magenta is added, and as soon as this is completely dissolved the temperature is raised as rapidly as possible to  $465^{\circ}$  F., the point of ebullition of the hydrochloride, at which it is maintained until the violet-red coloured mass suddenly becomes a maroon. This point is usually reached in the course of one or two hours; yellowish vapours of a peculiar alliaceous odour, recalling that of phenyl cyanide, making their appearance just before the change above-mentioned takes place. The colour is soluble in water, alcohol, and acids, and may be employed directly for dyeing, or it may be purified by precipitating its aqueous solution with common salt. It gives rich shades on silk, and also on leather. It is not improbable that this colouring matter is an impure chrysotoluidine derivative.

Schultz prepares a fine garnet colour by passing a current of nitrous acid into finely divided rosaniline, suspended in a solution of soda or ammonia. It dyes wool, silk, and mordanted cotton full rich shades, varying from puce to garnet.

There is also a brown met with in commerce, manufactured from phenylenediamine by treating it with an alkaline nitrite. The phenylenediamine for this purpose is

In order to prepare it for use, 5 lbs. of the dye are dissolved in  $4\frac{1}{2}$  gallons of alcohol, and  $6\frac{1}{2}$  gallons of water are added, with constant stirring. It is then put aside to settle, and the clear brown solution decanted.

Most of the aniline browns are soluble in boiling water, and may be used directly for dyeing. No mordant is required for dyeing wool or silk: with cotton, albumen is employed, and also processes similar to those already described when treating of the other aniline colours. A yellower shade can in most cases be obtained by employing a small amount of picric acid; whilst for a redder shade magenta may be added to the bath.



## ANILINE BROWN.

ANILINE BLACK.—This colouring matter is of a very indefinite nature, and differs remarkably from the other aniline colours previously described, as it is quite insoluble in water and alcohol, in soap lye, and in acid or alkaline solutions, so that it has to be formed on the fibre itself. It gives a deep velvety shade on cotton, which is changed to a dull green by the action of acids, and restored again to its original colour by alkaline solutions. Dilute solutions of potassium dichromate intensify the colour, and



acid and 1 of potassium chlorate, to which an alcoholic solution of magenta, containing 50 grammes to the litre, is added. The shade of brown may be altered by employing less oxalic acid and chlorate—this causes it to have a redder tinge. By adding neutral extract of indigo, any shade of colour up to black may be obtained.

This brown may also be fixed on cotton by means of albumen: it is prepared for this purpose by acting on magenta with hydrochloric acid and potassium chlorate. The product, which is insoluble in water, after being thoroughly washed, is ready for use. It is soluble in alcohol and in concentrated sulphuric acid, from both of which solutions it is precipitated by water.

Wise prepares a brown in the following manner: a mixture of equal parts of rosaniline and formic acid—to which may be added half a part of sodium acetate—is heated for several hours to a temperature which may vary from  $290^{\circ}$  to  $400^{\circ}$  F. It then forms an orange-red coloured mass, which, when cold, is thoroughly mixed with three parts of aniline and again heated for an hour or two, this time to about  $445^{\circ}$  F. When the reaction is complete, the brown-coloured product is dissolved in dilute hydrochloric acid, and the colouring matter precipitated by common salt.

Sieberg prepares a brown dye by the action of aniline on the mixture of crude violaniline, mauvaniline, and chrysotoluidine obtained as an insoluble residue in the magenta manufacture. For this purpose 10 lbs. of the residue are added to 20 lbs. of fused aniline hydrochloride, and the mass heated until the brown colour is fully developed, which may be ascertained by dissolving a sample in alcohol. As soon as the reaction is complete, the product is poured with constant agitation into 50 gallons of boiling water, in which 40 lbs. of crystallised carbonate of soda has been dissolved. The insoluble brownish-black tarry mass thus obtained is repeatedly washed with water.



on the aniline, produce the insoluble aniline black which remains fixed on the tissue.

The beauty and lustre of the black thus obtained caused it to be extensively adopted in England, France, Switzerland, and Germany; but the excess of acid and the copper chloride attacked the rollers and doctors of the printing machines so strongly, that the process fell into disfavour. Moreover, the mixture would not keep for any length of time at the ordinary temperatures, the reaction which produces aniline black taking place in the mixture itself, so that the colour, being no longer formed on the fibre itself, would not adhere. It is still used, however, for block printing.

Lauth succeeded in obviating this inconvenience by substituting the insoluble sulphide of copper for the acid chloride of copper, and in January, 1865, took out a patent for the new process.

|                         |              |
|-------------------------|--------------|
| Water .....             | 5 litres     |
| Starch .....            | 1000 grammes |
| Sulphide of copper..... | 250 „        |

This mixture was boiled, and allowed to cool. In the meantime a second mixture was prepared containing:—

|                             |              |
|-----------------------------|--------------|
| Water .....                 | 1850 grammes |
| Torrefied starch .....      | 1200 „       |
| Gum water .....             | 1000 „       |
| Aniline hydrochloride ..... | 800 „        |
| Chloride of ammonium.....   | 100 „        |
| Chlorate of potassium ..... | 300 „        |

When cold, the two mixtures were thoroughly incorporated, and printed in the usual manner. The black was developed by ageing for 24 hours at about 70° F. and then washing thoroughly. In this mixture, the sulphide of copper is gradually converted into sulphate by the oxidising action of the hydrochloric acid and potassium chlorate, and then acts as the chloride of copper does in Lightfoot's

hypochlorites slowly destroy it. If, however, an aniline black be submitted to the action of a solution containing a hypochlorite merely until it acquires a red shade, and is then washed and exposed to the air, it slowly becomes black again.

The processes for printing aniline black are very numerous and varied, the earliest being that employed by Mr. J. Lightfoot, of Accrington, in 1860, and for which a French patent was taken out in January, 1863. The peculiarity of this colour is, that it does not exist when printed on the fabric, but is gradually developed by the reactions which take place between the various substances composing the mixture that is printed. The first mixture employed consisted of:—

|  |                              |
|--|------------------------------|
| Starch .....                             | 1½ lbs. to 1 gallon of water |
| Aniline .....                            | 8 ounces                     |
| Hydrochloric acid .....                  | 8 „                          |
| Ammonium chloride .....                  | 4 „                          |
| Nitrate of copper solution (88° Tw.) ... | 2 „                          |
| Chlorate of potassium .....              | 4 „                          |

In the patent of 1863 this was considerably modified, the mixture to be printed consisting of:—

|                                       |          |
|---------------------------------------|----------|
| Aniline .....                         | 8 ounces |
| Hydrochloric acid .....               | 8 „      |
| Acetic acid .....                     | 20 „     |
| Perchloride of copper (88° Tw.) ..... | 8 „      |
| Ammonium chloride .....               | 4 „      |

This was mixed with 1 gallon of starch paste containing 4 ozs. of chlorate of potassium in solution; or, if used for dyeing, the thickening could be omitted. The dyed or printed goods were then aged for three days, washed, and soaped, or passed through a dilute solution of chloride of lime, whereby an intense black was produced. During the ageing, the acid decomposes the chlorate of potassium, and the liberated chloric acid and the cupric chloride, reacting

|                            |             |
|----------------------------|-------------|
| Water .....                | 300 grammes |
| Starch .....               | 36    "     |
| Aniline .....              | 20    "     |
| Chlorate of potassium..... | 15    "     |
| Acetate of copper .....    | 15    "     |
| Nitric acid .....          | 10    "     |

Dullo has proposed to employ a paste prepared by mixing 100 grammes of aniline, 80 of hydrochloric acid, 10 of black oxide of manganese, and 1 litre of water. The colour, which is green at first, is changed to black by the action of ammonia.

The action of oxide of manganese on an acid salt of aniline has been taken advantage of by Lauth, who proposes to dye or print vegetable fabrics or yarns by first applying a salt of manganese, and then passing the goods through a bath of dilute caustic soda to precipitate the manganous oxide; this is finally converted into peroxide by treatment with chloride of lime. The mordanted pieces or yarn, after being thoroughly washed, are immersed in a bath of aniline salt containing 50 grammes of aniline, 100 of hydrochloric acid, and 150 of sulphuric acid to the litre of water. The mordanted parts then acquire a greenish hue, which becomes black when passed through a bath of soap lye, or weak alkali. Treatment with a dilute solution of potassium dichromate, or with a mixture of potassium chlorate, ammonium chloride, and sulphate of copper (1 gramme of each to the litre) intensifies the colour. The goods are finally washed and boiled with soap. In order to dye wool, silk, or other animal substances, the peroxide of manganese mordant is deposited by immersing them in a bath of weak manganate or permanganate of potassium, and then dyeing them in the manner just described. This process gives a very brilliant black, but the mordanting is troublesome, and the dye is apt to rub off a little.



mixture. As the soluble salt of copper does not exist in the mixture when printed, but is only formed gradually on the fibre, it does not affect the rollers and doctors; moreover, the mixture can be kept for a considerable length of time in a cool place.

The sulphide of copper for this purpose is prepared by precipitating a hot solution of sulphate of copper, with sodium sulphide made by boiling flowers of sulphur in a solution of caustic soda. The black precipitate merely requires to be collected and washed, to be ready for use.

The nature of the acid which enters into the composition of the aniline salt is not a matter of indifference: neither the acetate nor the citrate give good blacks, whilst both the hydrochloride and nitrate give good results. The more acid the aniline salt is, the more rapidly does the colour develop, and the deeper is the shade; unfortunately, when a great excess of acid is used, it not only attacks the rollers but also injures the fibre.

M. C. Koechlin has modified Lauth's process by substituting tartrate of aniline for the hydrochloride; this has not only the advantage that it can be applied to the most delicate tissues, but it does not attack the mordants for other colours with which it may be mixed in printing. Koechlin's formula is:—

|                             |           |
|-----------------------------|-----------|
| Water .....                 | 10 litres |
| Starch .....                | 2 kilos   |
| Torrefied starch .....      | 2 „       |
| Aniline .....               | 2 „       |
| Chloride of ammonium .....  | 4 „       |
| Chlorate of potassium ..... | 1 „       |

Boil together until the mixture is homogeneous, and when cold add 1 kilo of sulphide of copper paste and 2 kilos of tartaric acid.

M. Sacc has succeeded in obtaining deep olive-browns with the following mixture:—

The printed goods, after ageing for 24 to 48 hours at a temperature of about 80° F., are passed, first through an alkaline bath at 170° F., and then through a soap bath. If the whites are dull, they may be brightened with weak bleaching liquor.

An aniline black paste, to be used for printing with albumen, may be prepared by warming to about 140° F. a solution of 40 grammes of potassium chlorate, 32 of ammonium chloride, 80 of sulphate of copper, and 80 of aniline hydrochloride in a litre of water. In a few minutes a powerful reaction sets in, and the mixture froths up. It is now left to itself for a few hours, and if the black is not fully developed it is again heated to 140° F., and then exposed in an open place for a day or two. It must be carefully washed until it is quite free from soluble salts. It is then ready for use.

Jarosson and Müller have patented a process for aniline black in which iron chloride is substituted for the copper salt usually employed, the cloth being mordanted with it by immersion in a bath prepared by dissolving 6 lbs. of iron in 2 gallons of water and 20 lbs. of hydrochloric acid, and then diluting it with water until it has a density of 12° Baumé. It is then aged for 12 hours. The mordanted calico or yarn is then winced in a bath containing for each 60 lbs. of cotton 6 lbs. of aniline and 10 lbs. of hydrochloric acid, to which is added a solution of 4 lbs. 3 ozs. of potassium chlorate in 6 gallons of water. The cloth is then heated for 3 to 5 hours in a closed vessel to a temperature of 90° F., which is gradually raised to 120° F., and the colour finally fixed by a bichromate bath.

Schlumberger has proposed to print aniline black with a mixture made by adding 10 per cent. of moist aniline ferrocyanide to a thickened mixture of aniline chlorate. The aniline ferrocyanide for this purpose is prepared by mixing 2 kilos of aniline with 2 kilos of hydrochloric acid

The following recipes, the two first of which are by Mr. Spirk, may also be found useful:—

|                             |              |
|-----------------------------|--------------|
| Water .....                 | 6 litres     |
| Aniline .....               | 1000 grammes |
| Chlorate of potassium ..... | 625 „        |
| Chloride of ammonium .....  | 625 „        |

Boil for a quarter of an hour, and, when nearly cold, add 1000 grammes of tartaric acid dissolved in 1 litre of water, stirring all the time.

To prepare this for use add 135 grammes of starch and 135 of dextrin to 1 litre of the mixture, and boil until dissolved; then, just before printing, add 60 grammes of sulphide of copper.

---

|                          |             |
|--------------------------|-------------|
| Water .....              | 3 litres    |
| Starch .....             | 150 grammes |
| Tragacanth .....         | 7½ „        |
| Dextrin .....            | 42 „        |
| Potassium chlorate ..... | 90 „        |
| Ammonium chloride .....  | 75 „        |

Boil until dissolved; when cold add 240 grammes of aniline, and, just before printing, 75 grammes of sulphide of copper.

---

|                          |             |
|--------------------------|-------------|
| Water .....              | 6 litres    |
| Starch .....             | 300 grammes |
| Tragacanth .....         | 150 „       |
| Torrefied starch .....   | 750 „       |
| Potassium chlorate ..... | 200 „       |

Boil until dissolved; when cold add 400 grammes of aniline hydrochloride, and, just before printing, 200 grammes of sulphide of copper.

---

|                             |             |
|-----------------------------|-------------|
| Starch solution .....       | 5 litres    |
| Dextrin solution .....      | 5 „         |
| Tragacanth solution .....   | 5 „         |
| Potassium chlorate.....     | 500 grammes |
| Aniline hydrochloride ..... | 1000 „      |

Before printing incorporate 330 grammes of sulphide of copper.



between the aniline hydrochloride, and the potassium chlorate.

Some aniline blacks resist the action of chemical agents extremely well, whilst others readily turn olive-green in contact with air containing sulphurous fumes, so that if the gas, used in a warehouse where goods dyed or printed with aniline black are stored, should contain a little sulphur, the folds of all the pieces will be turned green, more or less, by the sulphurous anhydride produced.

Aniline black may be considered as the result of the mixture of colours produced by two different reactions, namely, the decomposition of the aniline chlorate and of the oxidation of the aniline itself. By the decomposition of the aniline chlorate, chlorinated substitution products of aniline are formed, and the various degrees of substitution which may take place would offer a probable explanation of the different results obtained.

The presence of copper has generally been regarded as essential to the production of aniline black, but Mr. Lightfoot has recently ascertained that there are a few other metals which are capable of replacing it in this curious reaction. The manner in which the experiments were carried out was by printing a thickened mixture of ammonium chlorate and aniline hydrochloride, containing excess of aniline, on well bleached cotton by means of a wooden roller. The fabric thus prepared was brought, whilst still damp, in contact with various metals, and allowed to remain for a quarter of an hour, after which it was hung up in a warm moist atmosphere for twelve hours, and then passed through an alkaline bath. The metals tried were copper, iron, vanadium, uranium, nickel, lead, zinc, antimony, tin, manganese, chromium, bismuth, arsenic, titanium, tungsten, cadmium, molybdenum, mercury, silver, gold, platinum, palladium, rhodium, iridium, osmium, ruthenium, cobalt, aluminium, magnesium, thallium, lithium

of 19° Baumé, and then adding it to a solution of 2·4 kilos of potassium ferrocyanide in 4·2 litres of water. The ferrocyanide should be dissolved in the water by boiling, and as soon as it has cooled to 135° F. the aniline salt must be added. When it is quite cold, the crystalline pulp of aniline ferrocyanide is thrown on a filter and allowed to drain. It should weigh about 4·7 kilos. It has the inconvenience that it cannot be kept long, for it quickly acquires a violet colour, especially if exposed to light.

The composition of aniline black is not known, neither is its mode of formation thoroughly understood. It seems probable, however, that it consists of two colours, one a brown-black, produced by the action of the chlorinating agents on the aniline salt; the other, an intense violet blue-black, is, perhaps, a product of the oxidation of the aniline salt. The former is the most stable, resisting the action of almost all chemical agents; whilst the latter, although it resists soaping, is turned green by a trace of free acid. These two colours combined form ordinary aniline black.

According to Brandt, the composition of the aniline blacks fixed upon fibrous materials differs greatly according to the process employed, as is evident from the manner in which they withstand the action of light and of chemical reagents. The more intense the black, the better does it resist the agents which are likely to produce this change. A black which has been formed in the presence of an excess of aniline is always faster than one formed where the acid is in excess, the latter being apt to turn green. As, however, potassium chlorate decomposes but slowly in the presence of an excess of aniline, it is advisable to substitute for it, in this case, aniline chlorate; the development of the colour also takes place much more rapidly, since the chlorate of aniline itself is applied to the cloth, instead of being formed by double decomposition



powerful than aniline, and expels it from its salts; so that if a piece of cotton lightly dyed as above described, and then treated with an alkali, be immersed in a solution of aniline hydrochloride, it immediately takes a green tinge, even if the aniline is in excess. A piece of cotton moderately coloured with aniline black is a good test for the presence of free acids or alkalis, and the same piece may be used several times without losing its sensitiveness. When turned green by an acid, it should be well washed with distilled water, after which it will be found to change to violet when immersed even in a very feeble alkaline solution, such as spring water. When the greenish-black precipitate obtained by Rheineck's method is treated with concentrated sulphuric acid, it gives off hydrochloric acid, and yields a violet-coloured solution; on evaporation this leaves a green-black residue apparently the sulphate of the base.

In dyeing with aniline black, the nature of the aniline, as in the preparation of the other aniline colours, is a matter of considerable importance, neither pure aniline nor pure toluidine giving satisfactory results. The aniline oils usually employed for this purpose may be separated by fractional distillation into four portions.

1. About 60 to 65 per cent. of nearly pure aniline, boiling at  $356^{\circ}$  to  $365^{\circ}$  F.
2. About 18 to 22 per cent. of a mixture of aniline and toluidine, boiling at  $365^{\circ}$  to  $378^{\circ}$  F.
3. About 8 or 9 per cent. of nearly pure toluidine, boiling at  $378^{\circ}$  to  $388^{\circ}$  F.
4. From 4 to 6 per cent. of residue, boiling above  $388^{\circ}$  F., and consisting of xylidine, cumidine, &c.

The specific gravity of these fractions is as follows:—

1. From  $2^{\circ}.75$  to  $3^{\circ}.4$  Baumé.
2. „  $1^{\circ}.6$  to  $2^{\circ}.1$
3. „  $0^{\circ}.6$  to  $1^{\circ}.0$
4. „  $0^{\circ}.5$



lanthanum, didymium, erbium, yttrium, tantalum, and niobium, also selenium and tellurium. The result showed that the best black was produced by vanadium, the next best by copper, then uranium, and lastly iron. The other metals gave but little colour, or none at all.

It has been found that all the aniline blacks believed to be formed in those processes in which copper salts are not employed, owe their formation to the presence of that metal in the vessels in which the mixtures have been prepared, or to the use of copper or bronze rollers in printing; the merest trace of copper being sufficient to produce a black colour, although a larger quantity greatly facilitates its development. Mr. Lightfoot found that a sovereign or a shilling which had no effect on his printed calico, after having been violently shaken in a bag with some copper coins, produced a change; the gold coin giving a grey mark, and the silver one an almost black tint.

It has also been thought that the presence of chloride of ammonium was essential to the formation of the colour, but Rheineck has prepared aniline black without the use of ammonia, by mixing equal weights of aniline, hydrochloric acid, and potassium chlorate, with a minute quantity of chloride of copper, and a sufficient quantity of water, and allowing the solution to evaporate spontaneously. The black powder thus produced, after being thoroughly washed with water, left no residue on ignition.

According to Rheineck, aniline black is a powerful base, to which he gives the name of *nigraniline*. When a cotton fabric is immersed in a solution of aniline hydrochloride and potassium chlorate, containing a little cupric chloride, and then exposed to the air, it acquires a dark green colour, which on treatment with alkalis changes to a violet-black. The dark green compound is the hydrochloride of the base, from which the hydrochloric acid may be removed by soda or ammonia, leaving the black base. This base is more

obviate this inconvenience by cooling the solutions to the freezing point, but, as aniline chromate is comparatively insoluble at a low temperature, it crystallised out if the solutions were sufficiently concentrated to produce the colour, and, being deposited on the cloth, caused the formation of spots. Moreover, when the piece was removed from the bath and the temperature rose, there was danger of its being burnt in the neighbourhood of the spots, from the heat evolved in the decomposition of the aniline chromate.

M. J. Persoz has overcome these difficulties by the simple expedient of exposing the tightly stretched cotton fabric to the spray of solutions of an aniline salt and of potassium bichromate, which are separately applied to the cloth by means of a horizontal brush, to which a reciprocating motion is communicated in a vertical direction. These solutions, which may be thus applied either successively or simultaneously, become intimately mixed in the fabric itself, where the reaction takes place which results in the production of the black. The cloth has at first a very dark green colour, which changes to a pure black when washed and passed through a soap bath. By printing the fabric with resins or fats previous to dyeing it in this way, white patterns on a black ground may be obtained.

Persoz found that neutral salts of aniline do not give good results, neither do salts of organic acids, such as the acetate or oxalate; the best aniline salts for the purpose being the biacid salts. The sulphates give a reddish-black, and the hydrochlorides and nitrates a black with a violet or blue shade. As might be expected, a mixture of equal volumes of the bisulphate and bihydrochloride gives excellent results. It is necessary to employ a rather concentrated solution of bichromate of potassium, containing not less than 8 per cent. of the salt.

Aniline black is much valued for printing on cotton



Pure aniline oil of Coupier has a density of 3°.5 Baumé; ordinary toluidine 0°.88; and pseudotoluidine 0°.50. Pure aniline oil of Coupier, and anilines boiling at temperatures varying from 356° to 365° F., yield intense and brilliant blacks. Pseudotoluidine and the products boiling at 365° to 378° F., also give good blacks, but with a blue shade. Ordinary toluidine of Coupier, and fractions of aniline oil boiling above 378° F., give unsatisfactory shades between brown and black.

As toluidine, which is decidedly injurious to the colour if present in too large a quantity, has a comparatively low density, it will be evident that the specific gravity of the oil affords important indications of its value for the production of aniline black. If the specific gravity of the oil is above 3°.5 Baumé, it will generally be found to contain nitrobenzene. Anilines of 3°.5 to 2° Baumé give satisfactory blacks, whilst if below 2° it contains too much toluidine.

Although this method of testing the value of the aniline has the advantage of simplicity and rapidity, much more accurate results may be obtained by submitting the sample to fractional distillation, and noting the amount which distils over between 355° and 375° F.

Hartmann estimates the value of a given sample of aniline by observing the yield of black dye which it gives as compared with that obtained from a known quantity of Coupier's aniline.

Although it had long been known that bichromate of potassium has a very powerful action upon certain aniline salts if the solution is sufficiently concentrated, producing a black precipitate, yet none of the attempts to render this available for dyeing black have hitherto been successful. Thus, if the mixed solution of the aniline salt and bichromate is very dilute, the fabric immersed in it is not dyed at all; whilst, if concentrated, a black precipitate soon makes its appearance in the bath. Attempts were made to

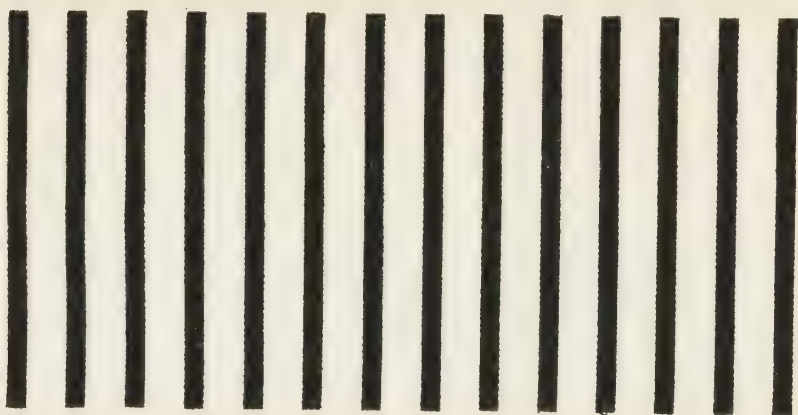


grammes of tartaric acid. The whole is well stirred up until the salts are completely dissolved.

The potassio-chromic tartrate is prepared by dissolving 960 grammes of potassium dichromate in 3 litres of boiling water, and when the solution has cooled to 110° F., adding 1,440 grammes of finely powdered tartaric acid. The vessel is placed in cold water, so as to avoid any rise of temperature, which might prove injurious. The printing should proceed continuously, and not stop, in fact, until the last piece leaves the dry plates. The pieces are hung up for forty-eight hours in a warm room, the temperature of which is about 105° F., then washed, dried, and finished. Paler shades may be obtained by diluting the mixture with gum water.

Casthelaz prepares an aniline grey by the action of aldehyde on an acid solution of mauveine, but its price hitherto has been very high. To prepare it, 10 lbs. of mauveine paste are dissolved in 11 lbs. of concentrated sulphuric acid 66° Baumé: 6 lbs. of aldehyde are gradually added, and the whole left to stand for four or five hours. It is then poured into water, the solution filtered, and the colouring matter precipitated by common salt. It may easily be purified by successive solutions and reprecipitations.

To prepare it for printing, one part of the solution of 'Casthelaz grey' is mixed with four of reduction paste made by boiling 1 gallon of acetate of alumina, 1 gallon of water, and 3 lbs. of starch until dissolved, and then adding 8 ozs. of arsenic dissolved in 1 pint of glycerin. The pieces should be steamed for half an hour.



ANILINE BLACK.

on account of its brilliancy and fastness. It acquires a greenish hue by long exposure to air and light, but the original colour is restored by treatment with alkaline solutions, or by washing with soap. Considerable difficulties have hitherto been met with in dyeing silk and wool with this colour, but in 1865 Mr. Lightfoot patented a process for treating wool, by which it was rendered capable of taking up aniline black. A solution is prepared with 1 lb. of chloride of lime to 1 gallon of water, and the wool is immersed at 100° F. in a bath of 30 gallons of water, 7 lbs. of solution of chloride of lime, and 1 lb. of hydrochloric acid, and worked in it until it acquires a yellowish tinge. It is then thoroughly washed, and is ready for dyeing by Lauth's or Lightfoot's process.

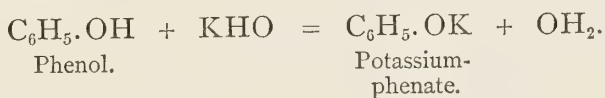
According to Laüber, an aniline grey may be printed on cotton by the following process:—

In 3·5 litres of water 625 grammes of potassium chlorate are dissolved, and on cooling the following materials are stirred in: 6·5 litres of gum water to 1 kilo; 312·5 grammes of ammonium chloride; 1500 grammes of potassio-chromic tartrate of 30° Baumé; 200 grammes of aniline; and 1160

draining and pressure, or by means of a centrifugal machine. If a very pure phenol is required, it is advisable to repeat the solution in alkali and precipitation with an acid before the final rectification. This precipitation should be made fractionally, the first portions which are thrown down containing all the naphthalene and most of the cresol, whilst the subsequent fractions consist of almost pure phenol, which will crystallise after one rectification, if a crystal of the substance be added to the distillate when cold.

Phenol,  $C_6H_6O$  or  $C_6H_5.OH$ , crystallises in long colourless needles, which melt at  $108^\circ F.$ , and boil at  $359.6^\circ F.$  It is moderately soluble in water, and forms with it a crystalline hydrate,  $2C_6H_6O + OH_2$ , in large six-sided prisms, which melt at  $93^\circ F.$  When a small quantity of water is added to crystalline phenol, it takes it up and becomes an oily liquid. It is miscible in all proportions with alcohol, ether, and strong acetic acid.

Phenol is very closely allied to aniline and to benzene,  $C_6H_6$ : it may be regarded as derived from the latter by the replacement of one atom of hydrogen by the group  $OH$ , thus:  $C_6H_6O = C_6H_5.OH$ . This atom of hydrogen is replaceable by metals, so that when treated with an alkali, such as potassium hydrate, the hydrogen is replaced by potassium.



The compounds, with the metals of the alkalis and the alkaline earths, are very readily soluble in water; advantage is taken of this in the process of extracting phenol from coal-oil by agitating it with an alkaline solution: the sodium or calcium phenate dissolves, and on the addition of an acid to the solution, it is decomposed; a sodium or calcium salt being formed, whilst the phenol separates as an oil if the solution is sufficiently concentrated.



## CHAPTER XVI.

### PHENOL, CRESOL, AND NAPHTHALENE COLOURS.

Besides the numerous beautiful dyes which have been described in the previous chapters as derived from aniline and its homologues, there are others, which, although not 'aniline colours,' have been prepared from products obtained in the distillation of coal-tar. It is the object of the present chapter to notice briefly the various compounds in coal-tar which yield these colours, and also to describe the mode of preparation of the most important of the latter.

PHENOL.—This substance, which is known also by the name of carbolic acid or coal-tar creosote, was discovered in coal-tar by Runge, and was afterwards obtained in larger quantity and carefully examined by Laurent, and by Williamson and Scrugham. The first, however, to manufacture it on a large scale was Dr. E. Sell, a German chemical manufacturer at Offenbach, who introduced it as a substitute for creosote.

Phenol may be extracted both from the light coal-tar naphtha, and also from that portion of the oil which distils between 300° and 400° F. by agitating them with milk of lime or a solution of soda, the former source yielding the purer article. After separating the clear solution from the neutral oils, and neutralising it with an acid, the impure phenol is obtained as an oily layer, which is submitted to fractional distillation. The portions which come over between 360° and 368° F., when well cooled, form a mass of crystals, from which the fluid portions may be removed by

two rows on a sand bath. All these flasks communicate by means of tubes, with a large stone-ware vessel to condense the acid fumes. As soon as the drops of phenol no longer produce a violent reaction when they fall into the nitric acid, the supply is cut off, and a gentle heat is applied by means of the sand bath, to dissolve the resinous mass floating in the liquid. As soon as this is effected, the contents of the flasks are poured into a crystallising vessel, where the picric acid is deposited, partly in plates, and partly as a resinous cake at the bottom.

In order to purify the crude picric acid, after it has been collected and the acid mother liquor allowed to drain off as far as possible, it is dissolved in boiling water previously mixed with about one thousandth of sulphuric acid, and then filtered from the yellow resinous matters which are comparatively insoluble in the acid liquid. The picric acid separates from the solution, on cooling, in crystalline plates of a pale yellow colour. But these crystallisations cause the loss of a considerable quantity of substance, and the product is by no means free from tarry and resinous matters; moreover, the large quantity of water required to dissolve the acid renders the filtrations inconvenient.

Another process is therefore very generally adopted which consists in nearly neutralising a boiling solution of picric acid with sodium carbonate, and filtering from the resin, which is but very slightly soluble if the liquid be distinctly acid. On adding excess of sodium carbonate to the filtrate, nearly the whole of the sodium picrate crystallises out, being comparatively insoluble in strong solutions of the carbonate. The nearly pure sodium picrate thus obtained, after being freed as far as possible from adhering mother liquor, is dissolved in boiling water, and decomposed by a slight excess of sulphuric acid. The picric acid being nearly insoluble in the strongly acid solution of sodium sulphate, crystallises out almost entirely on cooling. After

*Picric acid.*—*Picric acid*, *carbazotic acid*, or *trinitrophenol* is the most important of the compounds obtained from phenol by the action of nitric acid on it. When phenol is treated with dilute nitric acid, taking care that no great elevation of temperature occurs during the reaction, a deep brown tarry mass is obtained, from which two isomeric *mononitrophenols*  $C_6H_5(NO_2)O$ , may be obtained; one of these crystallises in yellow needles, which are readily volatile in the vapour of water; the other forms colourless needles, which are not volatile at  $212^\circ F$ . By the further action of nitric acid on these compounds, another atom of hydrogen may be displaced by the group  $NO_2$ , and *dinitrophenols*  $C_6H_4(NO_2)_2O$  are obtained. Finally, the long continued action of nitric acid on any of these gives rise to *trinitrophenol* or *picric acid*,  $C_6H_3(NO_2)_3O$ , which may be regarded as phenol in which three of the hydrogen atoms have been displaced by  $NO_2$ .

Stenhouse's method of preparing this acid by the action of nitric acid on the resin of the *Xanthorrhæa hastilis*, or Australian 'yellow gum,' has been recommended by Cary Lea as one of the best modes of making it. It is now, however, universally manufactured from phenol, which for this purpose must be tolerably free from cresol, otherwise the product will be contaminated with nitro derivatives of that substance.

Concentrated nitric acid acts on phenol with extreme violence, so that in preparing picric acid it is necessary to operate with the dilute acid. Perra puts 6 parts of nitric acid, of density 1.3, into a flask or other suitable apparatus, furnished with a condensing tube, or cohobator, and gradually adds 1 part of phenol. The nitric acid which is volatilised, condenses and flows back into the flask, whilst the nitrous fumes, which are generated in abundance, pass off. Guinon allows phenol to drop slowly into flasks containing nitric acid of specific gravity 1.3, and arranged in



what affected by washing, especially if soap be used; mordanting the goods with alum and tartar tends to render the colour faster.



PICRIC ACID.

Picric acid is also used for precipitating aniline green in the process of purification; and in dyeing, to modify the shade of aniline greens, or along with extract of indigo or Prussian blue, for producing greens.

The affinity which picric acid has for animal fibres renders it useful for detecting cotton when mixed with wool in a fabric. It is merely necessary to plunge the fabric into a hot solution of picric acid, and then wash thoroughly in water; the wool takes a permanent yellow tinge, whilst the fibres of cotton remain unchanged. If the specimen is a dyed one, it is advisable to bleach it before applying the test. Picric acid is frequently mixed with various extraneous substances, such as alum, oxalic acid, borax, and sodium sulphate, the latter arising from unskilful manufacture. These may readily be detected by gently heating the sample with benzene, which dissolves the picric acid and leaves the foreign matters. Its value may also be estimated by making a comparative dyeing experiment with a sample of known purity.

being collected and washed with a little water, it is almost chemically pure, provided sufficient water was taken in the first instance to enable the sodium sulphate formed to remain in solution, otherwise some of this salt crystallises out along with the picric acid.

Picric acid may also be very conveniently prepared by acting with nitric acid on the phenolsulphonic acid obtained by mixing phenol and sulphuric acid in equivalent proportions; or, still better, by converting the phenolsulphonic acid into a sodium salt, and then treating this with nitric acid.

Picric acid crystallises in lustrous plates, which are of a very pale yellow colour when pure. It melts at  $252^{\circ}.5$  F., and at higher temperatures gives off suffocating fumes, and ultimately decomposes with a slight explosion. Its solutions redden litmus, and it has a very bitter taste. It dissolves in 86 parts of water at  $59^{\circ}$  F., and in 26 at  $170^{\circ}$  F. Its tinctorial power is very great, one part of the acid, according to Carey Lea, communicating a distinctly yellow colour to 30,000 of water. It is readily soluble in alcohol and ether; strong nitric acid also dissolves it, and the solution is not altered by boiling. Picric acid yields compounds with the metals, many of which explode with fearful violence when fired with a detonator. Sodium picrate is sometimes sold as aniline yellow, and serious accidents may arise if due care be not taken.

Picric acid dyes silk, wool, and other animal substances yellow, the depth of tint varying from a pale straw to a golden colour. It has, however, no affinity for vegetable fibres, such as cotton, flax, and hemp, on which it can only be fixed by the aid of albumen or some similar mordant of animal origin. Wool and silk may be dyed by plunging them into a hot bath of a strength sufficient to give the desired tone, and then washing thoroughly in water. The colour resists the action of light very well, but it is some-

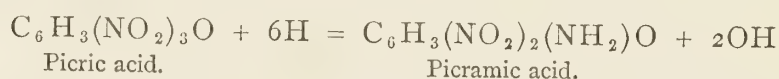


boiling water, into a solution of 2 parts of potassium cyanide in 4 parts of water at 140° F., with constant stirring. A powerful odour of ammonia and hydrocyanic acid is produced, whilst the solution acquires a deep reddish-brown colour, and, on cooling, forms a crystalline pulp of potassium isopurpurate. According to Kopp, a better process is to intimately mix powdered picric acid with twice its weight of potassium cyanide and a little water. After allowing it to stand for half an hour more water is added; the whole is then heated to 110° F., and allowed to cool.

The crystals obtained by either of these methods, after being drained and pressed, are purified by dissolving them in boiling water, filtering, and allowing the solution to cool. It then deposits *isopurpurate of potassium*,  $C_8H_4KNO_5$ , in brownish-red crystalline scales, with a metallic-green reflex, very similar to murexide. The potassium salt is only sparingly soluble in cold, but more readily in hot water. It is but very slightly soluble in a strong solution of potassium carbonate; and this circumstance may be taken advantage of to precipitate it from its solution if, owing to the presence of impurities, it does not crystallise out. The ammonium salt  $C_8H_4(NH_4)NO_5$  forms dark green crystals, with a metallic lustre, which, like the potassium salt, are but slightly soluble in cold water. This compound is isomeric with murexide or purpurate of ammonium, with which it was for some time supposed to be identical. Murexide, and the other purpurates however, are not explosive, whilst ammonium purpurate, when heated on platinum foil, deflagrates like gunpowder, and the corresponding potassium compound detonates sharply. Moreover, on adding hydrochloric acid to a somewhat concentrated solution of murexide, it becomes colourless; and on allowing it to stand, a substance called dialuramide crystallises out. A solution of an isopurpurate treated in a similar manner, becomes yellowish-brown, and turbid; and on



By the action of reducing agents on picric acid, a new compound, *picramic acid*, or *amidodinitrophenol*,  $C_6H_3(NO_2)_2(NH_2)O$ , is produced. It may be regarded as derived from picric acid by the displacement of one of the  $NO_2$  groups by  $NH_2$  thus:—



It may be prepared by passing sulphuretted hydrogen through a solution of picric acid in alcoholic ammonia. The liquid acquires a dark red colour, and, on standing, deposits a mass of deep reddish-brown tables of ammonium picramate, from which the acid may readily be obtained by dissolving it in hot water, and precipitating with a slight excess of acetic acid. Aqueous ammonia cannot be substituted for the alcoholic solution in this method of preparation, as in that case the reduction goes farther, and *diamidodinitrophenol*,  $C_6H_3(NO_2)(NH_2)_2O$ , is formed. Picramic acid may also be obtained by the action of other reducing agents on picric acid, as when an alkaline solution is heated with grape sugar, or by dissolving 1 part of picric acid and 7 of ferrous sulphate (green vitriol) in boiling water, and then adding a boiling solution of barium hydrate in slight excess.

Picramic acid crystallises from its aqueous solution in red needles, and from an ethereal one in garnet-coloured prisms. It melts at  $329^\circ F.$ , and decomposes at a higher temperature. It is almost insoluble in water, but soluble in alcohol and ether. It not only combines readily with bases to form salts, but it also unites with acids; the latter compounds, however, are not very stable.

Both picramic acid and its salts readily dye silk and wool, but they have not come into general use.

*Isopurpuric acid*, or *picrocyamic acid*. Hlasiwetz's method of preparing the potassium compound of this acid consists in pouring a solution of 1 part of picric acid in 9 parts of

any phenol comes over, and the non-volatile, brown, pitchy matter is dissolved in alcohol: to this solution milk of lime is added, which precipitates calcium brunolate, whilst calcium rosolate remains in the rose-coloured solution. On distilling off the alcohol and putting the residue aside, rose-coloured crystals of the lime salt are deposited, and from this, after purification, the rosolic acid may be obtained by precipitating the aqueous solution with acetic acid.

As it seemed probable that rosolic acid was produced by the oxidation of phenol or cresol, or a mixture of the two, Dr. Angus Smith proposed to prepare it by heating to a high temperature, a mixture of 2 parts of commercial phenol, with 1 of caustic potash, and 5 of black oxide of manganese. The product is then extracted with water and the rosolic acid precipitated by hydrochloric acid.

Tschelnitz mixes heavy coal-tar naphtha with slaked lime, and exposes it to the air for several months. The red mass thus obtained, is then treated in a manner similar to that originally employed by Runge.

The name rosolic acid, however, has also been applied to various other substances of totally different composition and properties, especially to the product now called *Corallin*, obtained by heating phenol with a mixture of sulphuric and oxalic acids, and also to that produced by the action of nitrous acid on rosaniline, and which Fresenius has proposed to name *pseudocorallin*.

*Corallin*.—In order to prepare this colour, which was discovered by Kolbe and Schmitt,\* 2 parts of oxalic acid, 3 of pure phenol, and 4 of sulphuric acid are heated together at 285° to 300° F. for five or six hours, in a vessel furnished with a cohobator. The dark brown-red mass thus obtained is poured into hot water, when a resinous substance separates having a cantharides-green lustre, whilst the supernatant liquid is a yellowish-red. The mixture is

---

\* Ann. Chem. Pharm., cxix., 169.



standing, brown amorphous flocks separate. The products of the decomposition of the isopurpurates are colouring matters, dyeing silk of a shade similar to the aniline browns known as Vesuvian and Bismarck.

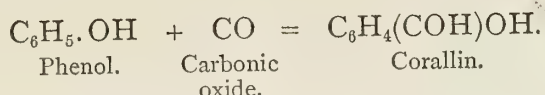
Isopurpurate of ammonia has been manufactured by Messrs. Roberts and Dale, of Manchester, and gives with silk, wool, and leather, beautiful shades of reddish-purple; its employment, however, is but limited. As the isopurpurates, when dry, explode readily, and with fearful violence, they should be made into a paste with water and glycerin, which keeps them moist.

The mordants used in dyeing with the isopurpurates are the same as those employed with murexide, the best being mercury and lead salts. Murexide gives, with mercury, a splendid purple with a violet shade; whilst with isopurpurates the purple has a reddish hue: the colours produced by the latter are much faster than those obtained with murexide, being acted on neither by sunlight nor by sulphurous acid. Silk mordanted with zinc gives a fine yellow with murexide, and a dark reddish-brown with the isopurpurate. Murexide colours are completely destroyed by acids and by alkalis, whilst those of the isopurpurates merely assume a yellowish tint. In dyeing, isopurpurate of aniline gives good results: this is made by dissolving in the bath 42 parts of aniline hydrochloride for every 100 of potassium isopurpurate. In this bath, silk mordanted with alum acquires a deep garnet-brown; and wool, which has been mordanted by boiling for two hours with 4 parts of alum and 1 of cream of tartar, becomes chesnut-brown.

ROSOLIC ACID.—This name was first given by Runge to a red colouring matter which he obtained from coal-tar. On agitating coal-tar naptha with milk of lime, and then adding an acid to the clear aqueous liquor, a mixture of impure phenols with rosolic and brunolic acids is obtained. This mixture is distilled in a current of steam as long as



### CORALLIN.



Persoz uses less sulphuric than Kolbe and Schmitt, the proportions being 2 parts of oxalic acid, 3 of phenol, and 2 of sulphuric acid, which are heated for several hours. The mass effervesces, becomes thick, and acquires a deep red colour: the reaction may be considered as terminated when a drop of the mixture dissolves in dilute aqueous ammonia with a deep red colour. It is then poured into water and treated in the manner above described.

Sulphuric acid is not essential to the production of this colour; it merely acts as a dehydrant, and may be replaced, although not with advantage, by boric, arsenious, or arsenic acids. In fact, Prud'homme found that rosolic acid was produced in small quantity if dry phenol were heated with carefully dried oxalic acid.



AURIN.

Corallin gives a variety of fine red shades, which are easily modified by the use of proper reagents, but its liability to change renders it somewhat difficult to fix the colour on the fabrics to which it is applied. It may, however, be printed with albumen or lactarine: 8 ozs. of

then boiled until the odour of phenol, which the vapour has at first, ceases to be perceptible, and, on cooling, the liquor deposits a quantity of orange-red flocks, which together with the insoluble portion are collected and washed.

In order to obtain corallin in the crystalline state,\* it is rubbed up with magnesia, and the mass exhausted by repeatedly boiling it with water. To the filtrate, ammonium chloride is added, when a small quantity of ammonia is given off, and a brilliant crimson precipitate is produced. This is treated three or four times successively with magnesia and precipitated with chloride of ammonium, so as to render the magnesian compound pure. If this is now decomposed by hydrochloric acid, and the precipitate dissolved in boiling alcohol, the pure corallin separates on cooling in long, slender, lustrous, scarlet needles. It crystallises from glacial acetic acid in transparent, dark red, rhombic prisms. Its melting point is  $313^{\circ}$  F. It is only slightly soluble in cold water, but more readily when it is boiling, giving a yellow solution. If an alkali, or an alkaline earth, or one of their carbonates be added, water takes up more of the substance and acquires a beautiful purple-red colour. The addition of potassium ferricyanide to the alkaline solution renders it much darker if the corallin be impure, but does not change it if pure. It dissolves readily in alcohol, ether, and in acetic acid with deep yellow colour. It is also soluble in phenol.

According to Fresenius, this compound has the formula  $C_{40}H_{38}O_{11}$ , but as it is undoubtedly produced by the action of nascent carbonic oxide on phenol, Kolbe suggests that it may be formylated phenol  $C_7H_6O$ , or  $C_6H_4(COH)OH$ , which agrees with the results of the analysis nearly as well as the formula proposed by Fresenius. If Kolbe's view is correct, its formation would be represented by the equation:—

---

\* Fresenius, Jour. Prakt. Chem., v., 184.



communicates a red colour. Its alkaline solutions acquire a brown colour on exposure to the air.

The chemical nature of peonine is at present unknown, and from the very different results obtained in dyeing with the two substances it would seem to be different from corallin. Its method of preparation renders it probable that it is an amide or imide of corallin.

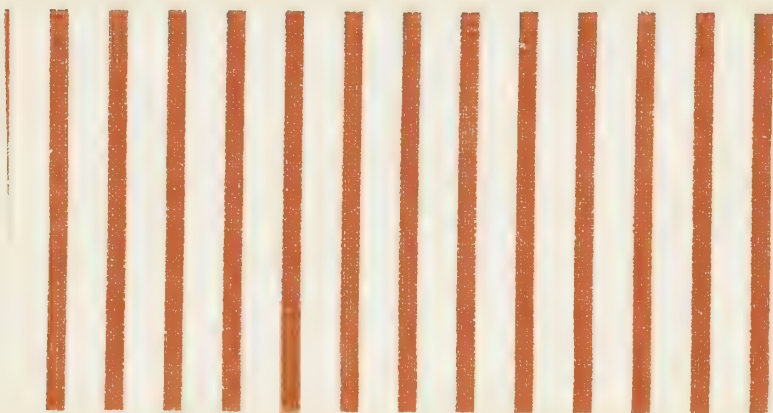
Red corallin is much used for dyeing wool, but it has the disadvantage that when it comes in contact with acids the red colour fades to yellow; this may be prevented, however, by the use of calcined magnesia, the corallin being dissolved in water or alcohol. The colour produced is a rich Turkey red, which maintains its intensity and brilliancy for years. This red shade can be produced at about two-thirds the cost of that from cochineal, and has the advantage that it is not turned blue by washing in water containing much calcium carbonate. The following is a good recipe for printing:—320 grammes of corallin are dissolved in 1 litre of water and 250 grammes of glycerin, and added to 560 grammes of magnesia suspended in 1 litre of water. This mixture is thickened with 3 litres of gum water containing 1500 grammes of gum, then printed, steamed, and washed in the usual way. For printing an orange-red with corallin, a lake is formed by dissolving 2000 grammes of corallin in a solution of soda at 10° B., diluting it with water, and after adding protochloride of tin, heating the mixture. The precipitate is mixed with:—

|                   |             |
|-------------------|-------------|
| Magnesia .....    | 100 grammes |
| Oxalic acid ..... | 260 „       |
| Gum .....         | 2000 „      |
| Water .....       | 10 litres   |

A bath for dyeing with corallin may also be prepared by dissolving the dye in alcohol with the help of a little soda, then pouring it into a large quantity of lukewarm



aurin solution added to 2 lbs. of lactarine dissolved in a mixture of 7 pints of water at 80° F. with 1 pint of ammonia, gives good results. After printing, the pieces should be steamed 20 minutes. The calcium and lime lakes of corallin are now largely employed by paper stainers.



YELLOW CORALLIN ON CALICO.

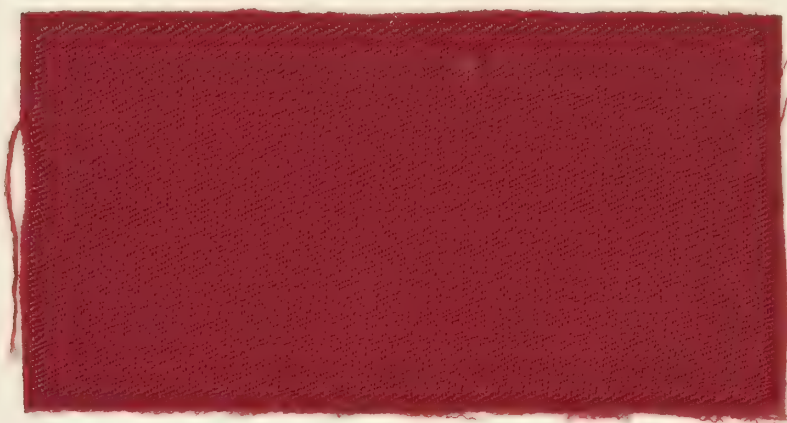
*Peonine*.—This colour, also called *red* corallin, is obtained from corallin by treating it with ammonia at a high temperature according to the method discovered by M. J. Persoz in 1859, and which was patented in France by Messrs. Guinon, Marnas, and Bonnet. In their process, 9 parts of crude corallin are introduced into a strong iron digester together with 22 parts of a concentrated solution of ammonia, and heated to 270° F. for three hours. On allowing the vessel to cool, and opening it, the corallin will be found to be completely dissolved in the ammonia, forming a thick liquid with a golden-crimson reflection. On adding an acid to this solution, a deep red precipitate of the colouring matter is obtained, which is capable of dyeing silk and wool of a red colour. Peonine is almost insoluble in water, but very soluble in alcohol, to which it

aniline and a little acetic acid, the solution soon assumes a pure blue colour, and on removing the excess of aniline by means of boiling dilute hydrochloric acid, a resinous substance is obtained consisting of a mixture of different bodies, some of which are soluble in acetic acid and in alcohol, and some insoluble. On heating the mixture of aniline and aurin for twenty hours to  $212^{\circ}$  F., a blue solution is obtained, which is also a mixture. A portion of the product dissolves in caustic soda with a purple colour, and is precipitated by acids in blue flocks, soluble in alcohol, and in acetic acid. The portion insoluble in alkalis dissolves completely in alcohol and acetic acid, with a fine blue colour; it is, however, only partly soluble in ether, the portion remaining undissolved being a dark blue powder with a golden reflection.

*Pseudocorallin*.—This is the name which Fresenius proposes to give to the compounds discovered by Caro and Wanklyn, and which they considered to be rosolic acid. It may be prepared by dissolving rosaniline or magenta in excess of hydrochloric acid, in such proportion that there may be three molecules of the acid to one of base, and then adding finely powdered potassium nitrite until the odour of nitrous acid no longer disappears on agitation. This converts the rosaniline into an azocompound, which, when boiled with dilute hydrochloric acid, decomposes with effervescence due to the escape of nitrogen, whilst red flocks separate; these, however, soon melt together and form a brown resinous cake, with a golden lustre. If perfectly pure rosaniline be used in this operation, the boiling mother liquor, poured off from the resinous cake, deposits a small portion of the pseudocorallin in well formed crystals, which after recrystallisation from alcohol closely resemble corallin in appearance. Caro and Wanklyn, who did not succeed in obtaining this compound in the crystalline state, assigned to it the formula  $C_{20}H_{16}O_3$ , and supposed it to be formed by the following reactions:—



water, and nearly neutralising it with tartaric acid. The goods are then entered, and worked for an hour and a half. Cotton must be mordanted with tin, and sumach or galls. The colour, which is a shade between cochineal and magenta, resists washing, but is affected by soap or exposure to sunlight.



CORALLIN ON WOOL.

*Azulin*.—This blue colour was discovered by Marnas, and patented by Messrs. Guinon, Marnas, and Bonnet. It is obtained by the mutual reaction of aniline and peonine. For this purpose, a mixture of 5 parts of peonine with 8 of aniline, are heated to the boiling point for several hours. The whole is thus transformed into a blue colouring matter, which is purified by washing it, first with dilute hydrochloric acid, then with hot coal-tar naphtha, and finally with a dilute solution of caustic soda. It is a violet powder with a golden iridescence, which is insoluble in water, but soluble in alcohol. According to Willm it has the composition  $C_{12}H_{12}NO_2$ , and may be regarded as dioxyphenylamide  $NH_2(C_6H_5O)_2$ .

A blue similar to, or identical with this, is also produced by treating aurin with aniline.\* When aurin is boiled with

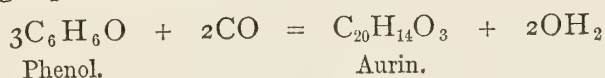
---

\*Jour. Chem. Soc., xxvi., 444.



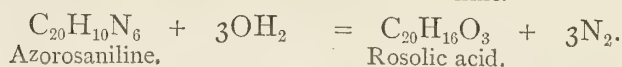
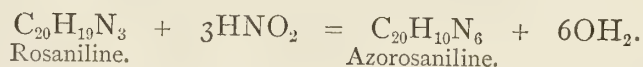
which is always made with an impure phenol containing cresol, it may be obtained in the pure state at once by heating to 230° F., for five or six days, a mixture of oxalic acid and pure crystallised phenol, pouring the product into water, distilling off the excess of phenol in a current of steam, and then dissolving the aurin in dilute caustic soda, and precipitating it with hydrochloric acid. The crystals only require to be dissolved in boiling alcohol and allowed to cool, when the pure substance separates in distinct needles.

The difference which undoubtedly exists between aurin and the corallin of Kolbe and Schmitt must be looked for in the difference of temperature at which the two substances are produced, namely, below  $230^{\circ}$  F. for aurin, and from  $285^{\circ}$  to  $300^{\circ}$  F. for corallin. The reaction which takes place in the formation of aurin may be represented by the following equation:—



Aurin forms crystalline compounds with sulphurous anhydride, and with the acid sulphites of alkalis. When an alkaline solution of aurin is heated with zinc dust, it becomes colourless, and the addition of an excess of hydrochloric acid then causes the precipitation of a new substance, *leukaurin*,  $C_{20}H_{16}O_3$ . When pure, it crystallises in thick, hard, colourless prisms, which are freely soluble in acetic acid.

Aurin, or yellow corallin, yields very fine orange shades on wool by printing with a lake prepared by dissolving 5 lbs. of yellow corallin in 2 gallons of caustic soda at 10° B., heated to a temperature of 140° F.; it is then diluted with 20 gallons of water, again heated until entirely dissolved, and rather more than 1½ pints of bichloride of tin at 55° B. added, previously diluted with 1 gallon of water. The precipitate is then collected, and allowed to drain. It should measure 4 gallons.



Fresenius, however, who has examined the pure crystalline compound, finds that it melts at  $316^\circ \text{F.}$ , and on analysis gives numbers corresponding with the formula  $\text{C}_{26}\text{H}_{28}\text{O}_{10}$ . It will be seen from this that Caro and Wanklyn's substance, pseudocorallin, is not identical with that obtained by Kolbe and Schmitt (corallin) by the action of sulphuric acid on a mixture of oxalic acid and phenol; moreover, an alcoholic solution of corallin is decolorised on the addition of a concentrated solution of acid sodium sulphite, whilst pseudocorallin undergoes no change.

*Aurin.*—There is a compound known in commerce by the name of yellow corallin, or aurin, and which is obtained by heating a mixture of phenol with oxalic and sulphuric acids in a manner similar to that employed in preparing corallin, but the temperature employed is lower. This colouring matter has been examined by Dale and Schorlemmer, who find that the commercial product is a mixture, from which they succeeded in extracting aurin by dissolving it in alcohol, and saturating the liquid with ammonia. A compound of ammonia and aurin is thus formed, which, being comparatively insoluble in alcohol, separates in the crystalline state. After being collected and washed with alcohol, it is treated with an acid, which removes the ammonia, and liberates the aurin. Aurin crystallises in slender red needles from concentrated hydrochloric acid, and from a mixture of alcohol and acetic acid, in dark red trimetric crystals; both these, however, obstinately retain a small quantity of water and acid. Aurin,  $\text{C}_{20}\text{H}_{14}\text{O}_3$ , when pure, does not melt even at  $422^\circ \text{F.}$ ; whilst corallin fuses at  $313^\circ \text{F.}$ ; moreover, the crystalline forms of the two substances are quite distinct.

Instead of extracting aurin from the commercial article,



of 5 parts of carbolic acid with 3 of arsenic acid in fine powder. In about two hours the reaction commences, and the mass acquires a yellow colour, which gradually increases in intensity. At the end of the twelve hours the temperature is raised to  $260^{\circ}$  F., at which it is maintained for six hours more. When cool, 10 parts of acetic acid at  $7^{\circ}$  B. are added; the product is dissolved in a large quantity of water, filtered, and the colouring matter precipitated by the addition of common salt. It may be purified by converting it into the barium salt and decomposing the latter with dilute sulphuric acid. When pure it forms reddish-brown scales or plates, which are readily soluble in water, alcohol, and ether. It dyes wool and silk yellow, and in presence of caustic or carbonated lime or baryta gives red shades, which are not affected by soap.

There is another yellow colour, known in commerce as 'Campo Bello yellow,' which is prepared from carbolic acid, by a secret process in the possession of Messrs. Schraeder and Berend, of Schönfeld, Leipzig. It is soluble in water, and dyes wool various shades of yellow: it is usual to add alum to the bath in the proportion of 3 lbs. to every 50 lbs. of wool.

CRESOL COLOURS.—Two yellow colours occur in commerce, known under the names of 'gold yellow' and 'Victoria yellow.' They are both impure salts of dinitrocresols. The former, '*goldgelb*' or 'gold yellow,' is a brown crystalline mass, which detonates sharply when heated; it is the potassium compound of a dinitrocresol,  $C_6H_2(NO_2)_2CH_3.OH$ , which when pure melts at  $180^{\circ}$  F. The free dinitrocresol may be obtained by strongly acidulating an aqueous solution of the yellow dye with sulphuric acid and then agitating it with ether, which takes up the liberated dinitrocresol and deposits it again in the crystalline state on evaporation. It crystallises readily from boiling water,



|                      |           |
|----------------------|-----------|
| Corallin paste ..... | 2 gallons |
| Powdered gum .....   | 4 lbs.    |
| Oxalic acid.....     | 11 ounces |

The mixture is heated until the gum and oxalic acid are completely dissolved, when it is ready for printing.

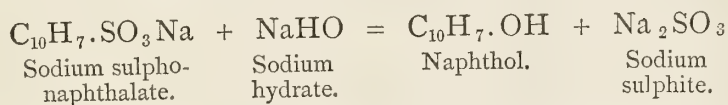
An orange-red shade may be obtained by dissolving the aurin in dilute ammonia so as to make a solution of 32° Tw. This solution is then mixed with 4 parts of starch paste, containing 14 lbs. to the gallon, printed, dried, and steamed for one hour.

*Phenicienne, or Rothine.*—This colour, which is also prepared from commercial carbolic acid, was discovered by Roth in 1863. It is made by gradually adding to carbolic acid a mixture of nitric acid of density 1.35 with twice its volume of sulphuric acid. The reaction is very violent at first, so that only a very small portion of the acid must be added at a time, but larger quantities may be poured in afterwards in successive portions until red nitrous fumes cease to be given off; for this purpose about 10 to 12 parts of the mixed acids are required for 1 of carbolic acid. As soon as the reaction is complete, the product is poured into a large quantity of water, and the brown precipitate which is produced is thoroughly washed with water, which is a tedious process, occupying several days. The colour is very soluble in alcohol, ether, and acetic acid, also in alkaline solutions, but almost insoluble in water. It dyes silk and wool without a mordant, but cotton must be mordanted with tannin and stannate of soda. It cannot be employed in printing, as the process of steaming destroys the brilliancy of the colour. It yields shades varying from a deep garnet to a chamois, according to the strength of the solution, or the nature of the oxidising agents employed.

*Fol's yellow.*—This colour is obtained by heating in an open cast-iron pot for twelve hours, at 212° F., a mixture

but not unpleasant odour, melts at  $174^{\circ}.5$  F. and boils at  $423^{\circ}$  F. It is readily soluble in alcohol, ether, and benzene, but insoluble in water. Although it has such a high boiling point, it passes over readily with the vapour of water, or when distilled in a current of steam.

*Dinitronaphthol*.—Naphthalene readily dissolves in concentrated sulphuric acid when the two are heated together; the product consisting of a mixture of two isomeric *sulphonaphthalic* or *naphthalene sulphonic acids*,  $C_{10}H_7.SO_3H$ , in varying proportion. If the temperature be higher than  $320^{\circ}$  F., scarcely anything but  $\beta$ -naphthalene sulphonic acid will be formed, whilst at  $175^{\circ}$  F. the product is principally the  $\alpha$  modification. If the potassium or sodium compound of either of these acids is fused with excess of caustic soda, the  $SO_3H$  group is replaced by  $OH$ , and a corresponding *naphthol* is formed, thus—



On dissolving the product in water, and adding an excess of acid, the naphthol is precipitated as an oil which solidifies on cooling.

$\alpha$ -naphthol crystallises in small shining, colourless needles, which are easily soluble in alcohol or ether, and in alkaline solutions, but only slightly soluble even in boiling water. It melts at about  $203^{\circ}$  F.  *$\alpha$ -Dinitronaphthol*,  $C_{10}H_5.(NO_2)_2.OH$  cannot be procured by the direct action of nitric acid on naphthol, but if the naphthol be dissolved in concentrated sulphuric acid, whereby it is converted into naphthol-sulphonic acid, then diluted with water, nitric acid added to the solution, and the whole gently heated, it deposits the dinitronaphthol in the form of minute yellow needles. This process was patented by Wichelhaus and Darmstaedter in 1867.

The same compound is formed by treating naphthylamine,



and is also readily soluble in alcohol, ether, benzene, and chloroform. The potassium compound is only slightly soluble in cold water.

'Victoria yellow' is also a salt of a dinitrocresol, which may be obtained from the dye in a similar manner to that just described. The nitrocompound, however, is not identical, but only isomeric with that from 'goldgelb,' as it melts at a much higher temperature,  $230^{\circ}$  F. Neither of these colours is extensively used.

NAPHTHALENE COLOURS.—One of the most abundant of the compounds occurring in coal-tar is the hydrocarbon naphthalene,  $C_{10}H_8$ , so much so, that the heavier portions of the coal-oil, when subjected to a low temperature, become quite pasty from the large quantity of naphthalene deposited by them in the crystalline state. The gas mains also, especially in the immediate neighbourhood of the gas works, frequently become choked up by the crystals of naphthalene which form in them, and which are occasionally met with in large masses of dazzling whiteness. As this substance occurs in such abundance, many chemists have endeavoured to turn this waste product to account, by transforming it into colouring matters similar to those obtained from aniline. Unfortunately, however, most of the naphthalene colours want that brilliancy and purity of tone which is such a distinguishing characteristic of those derived from aniline.

*Naphthalene*.—This hydrocarbon volatilises very readily, so that it sublimes in colourless crystals on gently heating the mass obtained by draining and pressing the pasty naphthalene deposited from the heavy coal-oils when they are cooled. These, however, have a disagreeable odour, which according to Ballò is due to the presence of leucoline oil: this may be removed by heating the crystals with sulphuric acid, and then washing and resubliming the fused cake of naphthalene. When perfectly pure, naphthalene has a faint



to prepare, so that, although it dyes silk and wool a deep yellow, it has not come into use.

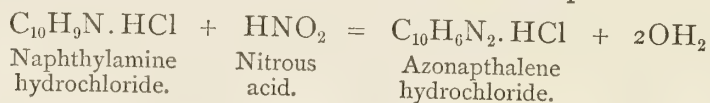
*Naphthylpurpuric acid.*—The naphthylpurpurates are prepared in a manner somewhat analogous to that employed for the isopurpurates, but the reaction should take place in an alcoholic solution. Dinitronaphthol is dissolved in 40 times its weight of boiling alcohol in a flask furnished with an inverted condenser, and a concentrated aqueous solution of potassium cyanide mixed with alcohol is gradually added. The orange-coloured potassium compound of binitronaphthol, which is at first formed, soon dissolves, and the boiling liquid acquires a deep brown hue. The solution is now concentrated by distillation, and the potassium naphthylpurpurate,  $C_{11}H_6KN_3O_4$ , which separates on cooling, is purified by pressure and recrystallisation from water. It forms brown, microscopic plates, which are very soluble in water, and have a slight green iridescence. The free acid has not been obtained.

*Indophane.*—This compound is also produced by the action of potassium cyanide on dinitronaphthol: for this purpose 6 parts of the nitro compound are dissolved in 400 of boiling water by the aid of ammonia, and to this, a hot concentrated solution of 9 parts of potassium cyanide is gradually added. As soon as the precipitation is complete, the product is thoroughly washed with boiling water, and the violet-coloured mixture of free indophane and potassium indophane is boiled with very dilute hydrochloric acid to remove the potassium, washed until free from acid, and dried.

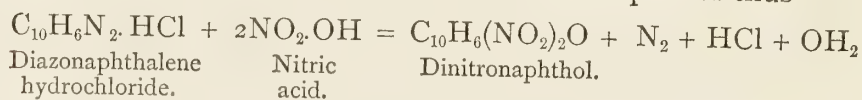
Pure indophane,  $C_{22}H_{10}N_4O_4$ , has a violet colour and a brilliant green iridescence. It is insoluble in water or alcohol, but moderately soluble in concentrated sulphuric acid, yielding a purple-red liquid.

*Resorcin-indophane*, a substance analogous to that just described, is formed when trinitroresorcin (styphnic acid)

first with nitrous acid, and then with nitric acid, a method previously patented by Martius. He adds a slight excess of potassium nitrite to an acid solution of naphthylamine, whereby diazonaphthalene hydrochloride is produced—



If this compound were boiled with hydrochloric acid,  $\alpha$ -naphthol would be produced, but if nitric acid is substituted for hydrochloric acid, the naphthol at the moment of its formation is converted into dinitronaphthol thus—



The  $\alpha$ -dinitronaphthol crystallises out in yellow needles which, if required quite pure, may be converted into the ammonium salt, and then after repeated crystallisation again decomposed by an acid. According to Ballò, it may also be prepared by heating 1 part of naphthylamine with 5 parts of nitric acid of density 1.35, and when all action has ceased, diluting the mixture with water and boiling. This nitro-compound forms beautiful crystalline compounds with the alkalis and alkaline earths. The lime salt is manufactured on a large scale by Messrs. Roberts and Dale, of Manchester, and is known as 'Manchester yellow' or 'Martius' yellow.' Its tinctorial power is even greater than that of picric acid, and it gives a very pure gold colour on silk and wool without the slightest tinge of green, which is so objectionable with picric acid. It also possesses the advantage over the latter that it is not volatile, so that it will bear steaming, and does not come off on other goods with which it may come in contact.

$\beta$ -naphthol.—This compound closely resembles  $\alpha$ -naphthol, and is formed, as has been already noticed, by fusing potassium  $\beta$ -naphthalene-sulphonate with excess of caustic soda. It likewise yields a nitro derivative, but it is difficult



decomposed, yielding a salt of chloroxynaphthalic acid,  $C_{10}H_5ClO_3$ , from which the free acid may be obtained by precipitation with hydrochloric acid. The pure acid is a pale yellow crystalline powder, which forms beautiful compounds with barium, zinc, and copper. It dyes wool of a scarlet colour without the aid of a mordant. Some of the salts of this acid are beautiful pigments. The preparation of this acid and its salts has been carried out on a large scale by Messrs. P. and E. Depouilly.

*Carminaphtha*.—This compound was first obtained by Laurent by acting on naphthalene with a mixture of potassium dichromate and sulphuric acid, but the exact circumstances under which it is formed have not been fully investigated. It is of a carmine-red colour, almost insoluble in water, but readily soluble in alcohol. It is a substantive colour on wool and silk, giving orange-red and red-violet shades.

*Nitroxynaphthalic acid*.—This compound, also called French yellow and chryseic acid, was discovered by Durant and Gelis. It may be prepared by heating to  $300^{\circ} F.$ , in a current of air, a mixture of 20 parts of nitronaphthalene, 50 of slaked lime, and 15 of potassium hydrate dissolved in the smallest possible quantity of water. In ten or twelve hours the mass will have assumed a deep yellow colour, and the reaction may be considered as completed. On extracting the product with water, a reddish-yellow solution is obtained. This, when concentrated, and strongly acidulated with hydrochloric acid, deposits the colouring matter as a yellow magma, which should be washed with water and dried. It dissolves easily in acetic acid, alcohol, and hot water, and may be obtained in fine golden-yellow needles, which are not volatile. It dyes silk and wool a full golden-yellow.

*Naphthylamine*.—This base, which bears the same relation to naphthalene that aniline does to benzene, is prepared by



is treated with potassium cyanide. Schreder\* prepares it by gradually adding 1 part of potassium cyanide dissolved in 5 of water at  $110^{\circ}$  F. to a solution of 5 parts of potassium styphnate in 50 of water at  $170^{\circ}$  F., maintaining the mixture at that temperature for ten or fifteen minutes; the liquid is then quickly filtered through linen, and the potassium compound of resorcin-indophane, which separates, collected, and washed with cold water until the wash water begins to have a green colour. On adding dilute sulphuric acid to a warm concentrated solution of this salt, and allowing it to cool, impure resorcin-indophane crystallises out in slender needles. It may be purified by dissolving the pressed crystals in hot water, filtering, and adding strong hydrochloric acid to the clear solution.

Resorcin-indophane,  $C_9H_4N_4O_6$ , forms small needles with a bronze iridescence, insoluble in alcohol, but very soluble in water, yielding a solution of a pure blue-violet colour; it is also soluble in cold concentrated sulphuric acid, but is precipitated again unaltered on the addition of water. *Potassium resorcin-indophane*  $C_6H_2K_2N_4O_6 + OH_2$  crystallises in microscopic needles, which dissolve with difficulty in cold, but readily in boiling water, with a pure green colour similar to that of potassium manganate. The concentrated aqueous solution gelatinises on cooling, but if potash be added, the salt separates in the crystalline state. It is insoluble in alcohol, and when strongly heated decomposes with explosion.

*Chloroxynaphthalic acid*, or *chloroxynaphthaquinone*.—When naphthalene is treated with potassium chlorate and hydrochloric acid it is converted into a mixture of monochloronaphthalene and dichloronaphthalene, and this product, if boiled with nitric acid, yields phthalic acid and chloroxynaphthyl chloride. When the latter compound is boiled with a dilute alkaline solution, it is

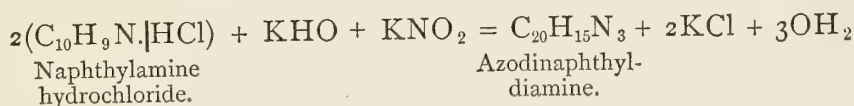
---

\*Ann. Chem. Pharm., clxiii., 297.

terminated, and the product is cool, it is mixed with 2 parts of quicklime, introduced into a retort, and submitted to distillation, either *per se* or in a current of steam. Ballò prefers to decompose the product with a solution of caustic soda, and then distil by means of steam.

Naphthylamine crystallises in white silky needles, which soon acquire a purplish-brown tint on exposure to the air. Its odour, which is most disgusting, is exceedingly persistent. It melts at 122° F., and boils above 570° F. It is almost insoluble in water, but is readily soluble in alcohol or ether, and in acid solutions. It is readily sublimable.

*Azodinaphthyldiamine*,  $C_{20}H_{15}N_3$ , is a base which was discovered by Perkin and Church, and is formed by treating naphthylamine hydrochloride with a mixture of potassium hydrate and nitrite, the reaction being:—



In preparing the substance, however, regard must be had to the state of concentration of the solutions, and the temperature at which the operation is performed; for if a moderately concentrated solution of the potassium hydrate and nitrite be added to a solution of the naphthylamine hydrochloride, saturated at 63° F., and which contains 35 grammes of the salt per litre, the product is mixed with a large amount of resinous matters; whilst, if the solution be too dilute, the potash precipitates unaltered naphthylamine. On this account Lecco\* advises that a preliminary trial should be made with small portions of the solutions, and when the precipitate is a brownish-red the solutions may be considered to have the proper degree of concentration for the given temperature. If they are too strong the precipitate will be dark brown. This precipitate is purified by dissolving it in a boiling mixture of alcohol and ether,

---

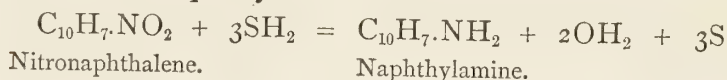
\* Deut. Chem. Ger. Ber., vii., 1290.



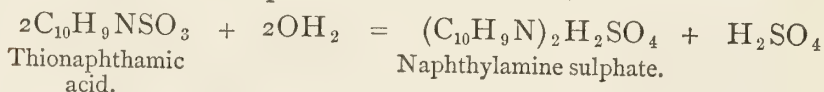
processes very similar to those employed in manufacturing the latter.

Naphthylamine,  $C_{10}H_9N$  or  $C_{10}H_7.NH_2$ , was discovered by Zinin in 1842, when acting on nitronaphthalene by ammonium sulphide. The nitronaphthalene for this purpose was prepared by treating finely divided naphthalene at the ordinary temperature for five or six days with nitric acid of density 1.35, thoroughly incorporating the mixture from time to time, or more rapidly by heating the two substances together at  $212^\circ F.$  with constant agitation. The product is thoroughly washed and then strongly pressed. If required pure it must be crystallised from alcohol.

In Zinin's process the nitronaphthalene is dissolved in alcoholic ammonia, sulphuretted hydrogen is passed into the solution to saturation, and the whole is allowed to stand: sulphur is then liberated, and the nitronaphthalene is reduced to naphthylamine.



Piria succeeded in obtaining naphthylamine by first converting nitronaphthalene into ammonium thionaphthamate by boiling it with dilute alcohol and ammonium sulphite, and then heating the product with dilute sulphuric acid. Naphthylamine sulphate is then formed.

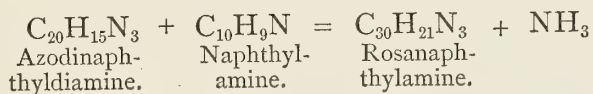


Roussin reduces nitronaphthalene by means of tin and hydrochloric acid, but by far the best method is that of Béchamp, by which, in fact, naphthylamine is now universally manufactured. For this purpose, 2 parts of nitronaphthalene are fused in a cast-iron pot heated on a sand bath, and 2 parts of iron turnings are added, and the whole thoroughly mixed. The pot is now taken off the bath, and 2 parts of acetic acid are poured in, when a powerful reaction takes place. As soon as this has



which may be rendered sufficiently pure for the purposes of the dyer by two successive solutions in dilute acid, and reprecipitations by salt. The crude product may also be purified by decomposing it with a slight excess of a solution of soda, distilling off the unaltered naphthylamine in a current of steam, dissolving the residual base in hydrochloric acid, and precipitating with salt in the manner just described. This colour is prepared on a large scale by Scheurer-Kestner, and by Durand and Hugenin, of Basle.

The base itself, *rosanaphthylamine*,  $C_{30}H_{21}N_3$ , has not been obtained in a pure state, but its composition may be inferred from that of its salts. Its mode of formation is as follows:



being precisely analogous to that which takes place in the formation of azodiphenyl blue by the action of aniline on azodiphenyldiamine. *Rosanaphthylamine hydrochloride*, when pure, forms large needles, with a green metallic reflex. They are only slightly soluble in cold water, more so in boiling water, and readily in hot alcohol. The free base, when treated with the iodides of methyl and ethyl, yields splendidly crystallised colouring matters.

By heating mixtures of azodinaphthyldiamine with aniline or with toluidine, Lecco has succeeded in obtaining new colouring matters very similar to 'Magdala red.'

*Naphthylamine violet*.—This colour is produced in a manner very similar to aniline black, but unlike the latter, it does not appear to be the final result of the oxidising process, but only an intermediate stage.

Kielmayer prints the following mixture:

|   |              |
|---|--------------|
| Starch .....                              | 456 grammes. |
| Water.....                                | 2500 „       |
| Naphthylamine .....                       | 118 „        |
| Hydrochloric acid (specific gravity 1.12) | 79 „         |

The naphthylamine is dissolved in the acid diluted with

filtering hot, and adding hot water until the liquid becomes turbid; on cooling, the azonaphthyldiamine is deposited in reddish-brown needles, which have a metallic-green iridescence. It melts at  $347^{\circ}$  F. according to Lecco ( $266^{\circ}$  F. Perkin), and is moderately soluble in alcohol, ether, and benzene; insoluble in water. The acid solutions are deep violet, but the original orange-red tint is restored on the addition of an alkali.

*Rosanaphthylamine*.—This colouring matter, which is also known as 'Naphthylamine red' and 'Magdala red,' appears to be produced when naphthylamine is treated with oxidising agents, such as mercuric nitrate or bichloride of tin; but the quantity formed is far too small to render these processes available for its manufacture.

The method adopted by Girard is to heat a salt of naphthylamine with a proper quantity of azodinaphthyldiamine, the proportions taken being:—

|                                     |        |
|-------------------------------------|--------|
| Powdered Azodinaphthyldiamine ..... | 6 lbs. |
| Naphthylamine .....                 | 6 „    |
| Glacial acetic acid .....           | 5 „    |

These materials are heated in a sand bath to a temperature of about  $340^{\circ}$  F., in a glass flask of the capacity of 2 gallons. The materials gradually dissolve, whilst ammonia is given off, and the mass acquires a red colour. Care must be taken to stop the operation as soon as a violet coloration begins to appear on the sides of the vessel. About 6 ozs. of glacial acetic acid are now added, and after thoroughly mixing, the contents are poured out on cast-iron plates and allowed to cool. To purify the crude product it is dissolved in 50 times its weight of water acidulated with hydrochloric acid, and carefully filtered through flannel. It is then exactly neutralised with sodium carbonate, and the colour precipitated by the addition of salt, as in the preparation of the aniline colours. This precipitate consists of crystals of impure rosanaphthylamine hydrochloride





part of the water ( $1\frac{1}{2}$  litres), then added to the starch, which has been boiled with the remainder of the water (1 litre), and the whole boiled for a few minutes: when cold,  $13\frac{1}{2}$  grammes of potassium chlorate dissolved in 300 grammes of water are added. The printed goods are aged for three days, then passed through a weak soda bath, and finally through a soap bath. The shade of colour produced is much affected, however, by the temperature of the oxidising room, which should be kept low, and the atmosphere should contain vapours of acetic acid.

Blumer-Zweifel makes a mixture for printing thus:—

|  |                   |
|--|-------------------|
| Gum water.....   | 1 litre.          |
| Naphthylamine .....                                    | 15 to 45 grammes. |
| Solution of chloride of copper at $51^{\circ}$ B. .... | 15 „              |

After printing, the fabric is aged for two or three days at  $77^{\circ}$  F., and then washed with soap. Fifteen grammes of naphthylamine gives a pale shade, 30 a medium shade, and 45 a deep shade. Alkalis render the colours reddish, whilst acids give it a blue tint.

Ballò has obtained a violet colour similar in every respect to Hofmann's violet, by heating magenta with monobromonaphthalene. The saturated alcoholic solution of the dye is of such a deep violet colour, that it appears almost black, whilst the addition of a small quantity of hydrochloric acid to the liquid, changes the colour to blue.

There are two other naphthalene colours, oxynaphthalic acid, and naphthazarin or dioxynaphthaquinone, the methods of preparation and properties of which have been already described when treating of alizarin (p. 55.); for it was at one time imagined that oxynaphthalic acid would prove to be identical with alizarin, whilst naphthazarin was, for some time after its discovery by Roussin, considered to be alizarin itself.



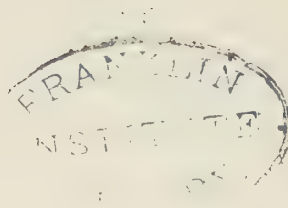
|  | PHYSICAL PROPERTIES.   | HEAT.  | WATER.  | ALCOHOL.   | CHLORINE.  | HYPOCHLORITE OF LIME.                 | CONCENTRATED SULPHURIC ACID.   | DILUTE SULPHURIC OR MURIATIC ACID.  | NITRIC ACID.   | ALKALIS.   | LIME AND BARYTA.  | ALUMINA AND ITS SALTS.  | PEROXIDE OF IRON AND ITS SALTS.   | SALTS OF LEAD.   | OTHER METALLIC SALTS.  | FERMENTS.   |
|--|--|--|---|--|--|---------------------------------------|--|---|--|--|---|---|---|--|--|---|
| Rubian<br>$C_{28}H_{34}O_{15}$         | Amorphous, shining, brittle, not deliquescent, dark yellow, and transparent in thin layers, very bitter. | Begins to be decomposed at 130° C., gives a sublimate of alizarin and much charcoal.   | Very easily soluble in water, removed from the solution by animal charcoal.   | Not so easily soluble in alcohol as in water; separated by alcohol from its combination with animal charcoal.          | Decomposed by chlorine, giving chlororubian and grape sugar.   | Decomposed, giving phthalate of lime. | Dissolved with a blood-red colour, and decomposed on boiling the solution with blackening.                                     | Decomposed on boiling, giving alizarin, rubiretin, verantin, rubiadin, and sugar. | Decomposed on boiling, giving phthalic acid.   | Gives blood-red compounds with alkalis; decomposed by excess of caustic alkali, giving alizarin, rubiretin, verantin, rubiadin, and sugar.   | With lime and baryta water dark red precipitates, soluble in pure water.  | Removed from its aqueous solution by excess of hydrate of alumina.  | ... ..  | With acetate of lead, alcoholic solution gives no precipitate; with basic acetate of lead it red precipitate.  | Alkaline solutions reduce salts of gold, but not salts of silver or copper.  | Not affected by yeast, or decomposed by casein, albumen, &c., but easily decomposed by erythrozym (the ferment of madder), giving alizarin, rubiretin, verantin, rubiadin, and sugar. |
| Alizarin<br>$C_{14}H_8O_4$             | Crystallises in long transparent dark yellow needles, with much lustre.                                  | At 100° C., loses its water of crystallisation and becomes opaque, at 216° C., begins to sublime, partly decomposes, leaving much charcoal.      | Slightly soluble in boiling water with a yellow colour.   | Soluble in boiling alcohol; solution is dark yellow, and when concentrated, deposits crystals on cooling and standing. | Decomposed by chlorine, and converted into a colourless substance.   | ... ..                                | Dissolved in the cold with a yellow colour, and not decomposed on boiling the solution.  | ... ..  | Decomposed by boiling nitric acid, giving phthalic acid.   | Dissolves in alkalis with violet colour; solutions in caustic alkalis do not change colour in the air; that in ammonia loses its ammonia.  | Ammoniacal solution gives with chlorides of calcium and barium, purple precipitates.  | Not more soluble in a boiling solution of alum than in boiling water; compound with alumina, not decomposed on boiling with weak caustic lye. | Peroxide of iron removes it from its solution in caustic potash or soda.  | With acetate of lead, alcoholic solution gives a purple precipitate, which on standing becomes red.  | Ammoniacal solution gives purple precipitates with salts of silver and copper; alcoholic solution becomes of beautiful purple with acetate of copper.  |   |
| Verantin<br>$C_{14}H_{10}O_4$          | Amorphous, pulverulent, reddish-brown.   | Heated in a tube gives a little sublimable and much charcoal.  | Almost insoluble in cold and boiling water.   | Soluble in boiling alcohol, and deposited again on cooling, as a brown powder.   | ... ..   | ... ..                                | Dissolved with a brown colour, and decomposed on boiling the solution with blackening.   | ... ..  | Decomposed by nitric acid on boiling, not by dilute acid.  | Soluble in alkalis with a dirty brownish-red colour.   | Ammoniacal solution gives precipitates with lime and baryta salts.  | ... ..  | ... ..  | With acetate of lead, alcoholic solution gives dark brown precipitate.   |  |   |
| Rubiretin<br>$C_{14}H_{12}O_4$         | Amorphous, resinous, brittle, opaque, dark brown.  | Softens at 100° C., then melts, then decomposes.   | Very little soluble in cold and boiling water.  | Easily soluble in cold alcohol.  | ... ..   | ... ..                                | Dissolved with a yellowish-brown colour, and decomposed on boiling the solution with blackening.                               | ... ..  | Decomposed by boiling nitric acid, and converted into a yellow substance, little soluble in alcohol.   | Soluble in alkalis with a brownish-red colour.   | ... ..  | ... ..  | ... ..  |  |  |   |
| Rubiadin<br>$C_{22}H_{24}O_{10}$       | Crystallises in bright lemon-yellow silky needles.   | Heated in a tube gives a little yellow crystalline sublimate and much charcoal.  | Tolerably soluble in boiling water, crystallises out again on cooling.  | Soluble in alcohol.  | Decomposed by chlorine and converted into perchlororubian. (?)   | ... ..                                | Dissolved with a yellow colour, and decomposed on boiling the solution with blackening.  | ... ..  | Dissolved by boiling concentrated nitric acid, without being decomposed.   | Dissolved with difficulty by alkalis, giving blood-red solutions.  | Ammoniacal solution gives with chlorides of barium and calcium.   | ... ..  | Soluble in perchloride of iron solution, but not converted into rubiacic acid.                                  | With acetate of lead, alcoholic solution gives no precipitate.   |  |   |
| Rubiadin<br>$C_{16}H_{12}O_8$          | Crystallises in yellow needles or in golden-yellow, glittering scales, or four-sided tables.             | When heated, entirely volatilises, giving sublimate of yellow, micaceous shining scales.   | Almost insoluble in boiling water.  | More soluble in alcohol than rubiadin.   | ... ..   | ... ..                                | Dissolved with a dark yellow colour, which changes to yellowish-brown on boiling.  | ... ..  | Decomposed by boiling nitric acid.   | Behaves like rubiadin.   | The baryta compound crystallises in dark brownish-red needles soluble in water.   | ... ..  | Insoluble in perchloride of iron.   | With acetate of lead, alcoholic solution gives no precipitate.   |  |   |
| Rubiadin<br>$C_{16}H_{10}O_8$          | Crystallises in greenish-yellow needles, or in tables with much lustre.                                  | When heated, entirely volatilises, giving sublimate of brilliant yellow scales.  | Slightly soluble in boiling water.  | Soluble in boiling alcohol and crystallises out on cooling.  | ... ..   | ... ..                                | Dissolved with a yellow colour; not decomposed on boiling the solution.  | ... ..  | Dissolved by boiling dilute nitric acid without being decomposed.  | Soluble in caustic alkalis, with a purple colour.  | Ammoniacal solution gives with chlorides of calcium and barium red precipitates.  | Removed from its alcoholic solution by excess of hydrate of alumina.  | Dissolves in perchloride of iron with a dark brownish-red colour, and converted by boiling into rubiacic acid.  | With acetate of lead, alcoholic solution gives a dark red precipitate.   |  |   |
| Rubiadin<br>$C_{16}H_8O_8$             | Lemon-yellow powder, not crystalline.  | When heated, gives no crystalline sublimate.   | Slightly soluble in boiling water.  | Slightly soluble in boiling alcohol.   | ... ..   | ... ..                                | Dissolved with a yellow colour, which becomes darker but not black on boiling the solution.                                    | ... ..  | Decomposed by boiling concentrated nitric acid.  | The potash salt crystallises on cooling of its solution in boiling water, in long silky, brick-red needles; the colour of its watery solution is red, but changes to purple on the addition of caustic potash; the salt is decomposed on heating, with a slight explosion. | Aqueous solution of the potash salt gives with chloride of calcium, a crystalline, orange-coloured precipitate, with chloride of barium a yellow precipitate. | Aqueous solution of the potash salt gives with alum an orange-coloured precipitate.   | Aqueous solution of the potash salt turns reddish-brown with perchloride of iron, but gives no precipitate.     | ... ..   | Aqueous solution of the potash salt gives with nitrate of silver a yellow precipitate, not changed on boiling the liquid; with sulphate of copper a red precipitate; with perchloride of mercury a yellow crystalline precipitate. |   |
| Rubiadin<br>$C_{16}H_8O_8$             | Crystallises in yellow shining needles and scales.   | When heated, gives a little crystalline sublimate.   | Very little soluble in boiling water.   | Soluble in boiling alcohol and crystallises out on cooling.  | ... ..   | ... ..                                | Dissolved, not decomposed on boiling the solution.   | ... ..  | Dissolved by boiling nitric acid, not decomposed.  | Soluble in caustic alkalis with a reddish-purple, in carbonated alkalis with a red colour.   | ... ..  | ... ..  | Dissolves in perchloride of iron with dark brownish-purple colour, and converted by boiling into rubiacic acid. | With acetate of lead, alcoholic solution gives a crimson precipitate.  | With acetate of copper, alcoholic solution gives an orange-coloured precipitate.   |   |
| Rubiadin<br>$C_{16}H_8O_8$             | Crystallises in yellow needles collected in grains and nodules.  | When heated, gives a little crystalline sublimate and much charcoal.   | Insoluble in boiling water.   | Easily soluble in boiling alcohol, not crystallising on cooling.   | ... ..   | ... ..                                | Dissolved with a reddish-brown colour, decomposed on boiling the solution with blackening.                                     | ... ..  | Dissolved by boiling nitric acid, solution on cooling depositing yellow shining needles.   | Soluble in alkalis with a blood-red colour.  | Soluble in lime and baryta water with blood-red colour.   | ... ..  | Very little soluble in perchloride of iron.   | With acetate of lead, alcoholic solution turns dark yellow, and after some time gives orange-coloured granular precipitates.   | With acetate of copper, behaves like rubiadin.   |   |
| Rubiadin<br>$C_{20}H_{30}O_{14}$       | Crystallises in lemon-yellow silky needles.  | When heated, gives a sublimate of alizarin and much charcoal.  | Soluble in boiling water and crystallises out again on cooling; watery solution is bitter and reddens litmus paper. | Soluble in alcohol.  | Decomposed slowly by chlorine, products of decomposition being soluble in water.   | ... ..                                | Dissolved with a dark red colour, which becomes reddish-brown on boiling the solution, a little sulphurous acid being evolved. | Decomposed on boiling, giving alizarin and sugar.                                 | Decomposed by boiling nitric acid, with facility.  | Dissolves in caustic alkalis with a cherry-red colour, which on boiling changes to purple, alizarin and sugar being formed; with carbonate of potash, gives silky puce-coloured needles of potash salt.  | Aqueous solution gives with lime water a light red precipitate; with baryta water a crimson precipitate.  | Aqueous solution gives no precipitate with acetate of alumina.  | Dissolves in perchloride of iron with a greenish-brown colour, the solution containing protochloride.           | With acetate of lead, alcoholic solution turns red without giving any precipitate; with basic acetate it gives a copious red precipitate.  | Alkaline solutions reduce salts of gold, but not salts of silver.  | Decomposed by erythrozym, giving alizarin and sugar.  |
| Chlororubian<br>$C_{22}H_{22}ClO_{12}$ | Crystallises in orange-coloured needles, slightly bitter on being chewed.                                | When heated, gives a little white crystalline sublimate and much charcoal.   | Soluble in boiling water and is deposited on cooling in amorphous masses.   | Soluble in boiling alcohol, crystallises out on cooling; solution does not redden litmus paper.                        | Converted by chlorine into perchlororubian.  | ... ..                                | ... ..   | Decomposed on boiling, giving chlororubiadin and grape sugar.                     | Decomposed by boiling nitric acid, giving colourless solution from which nitrate of silver precipitates chloride of silver.                                      | Soluble in alkalis with a blood-red colour; converted by excess of caustic alkali into oxyrubian, with loss of its chlorine.   | Aqueous solution turns red with lime water; with baryta water it turns red, and on boiling deposits red flakes and becomes colourless.                        | Aqueous solution gives no precipitate with acetate of alumina.  | Soluble in perchloride of iron with a brownish-yellow colour, becoming after some time dark brown.              | With acetate of lead, alcoholic solution gives no precipitate; with basic acetate, aqueous solution gives red precipitate.   | Aqueous solution gives no precipitate with nitrate of silver.  |   |
| Chlororubiadin<br>$C_{16}H_{11}ClO_4$  | Crystallises in small yellow needles and scales.   | When heated, gives acid fumes and a little crystalline sublimate, and leaves much charcoal.  | Insoluble in boiling water.   | Soluble in boiling alcohol, crystallises out again on cooling; solution reddens blue litmus paper.                     | Converted by chlorine into a dark yellow amorphous, resinous substance, insoluble in water, but easily soluble in alcohol. | ... ..                                | Dissolved with an orange colour, which becomes dark purple on boiling the solution.  | ... ..  | Dissolved by nitric acid, of sp. gr. 1.5; in the cold; the solution gives no precipitate with nitrate of silver, but on boiling chloride of silver precipitates. | Soluble in caustic fixed alkalis with a purplish-red colour, and in ammonia and carbonated alkalis with a blood-red colour.  | The baryta compound, formed by double decomposition, crystallises from water in long red needles, arranged in fan-shaped masses.                              | Alcoholic solution gives no precipitate with acetate of alumina.  | Insoluble in perchloride of iron.   | With acetate of lead, alcoholic solution gives no precipitate, even on adding ammonia also.  | Alcoholic solution gives with acetate of copper a copious light brown precipitate.   |   |
| Perchlororubian<br>$C_{22}H_2Cl_2O_7$  | Crystallises in colourless transparent, flat, four-sided iridescent tables.                              | When slowly heated, entirely volatilises, giving a sublimate of bright micaceous scales; suddenly heated it is decomposed with slight explosion. | Insoluble in boiling water.   | Soluble in boiling alcohol and crystallises out again on cooling.  | ... ..   | ... ..                                | Dissolved, not decomposed on boiling the solution.   | ... ..  | Dissolved by nitric acid, of sp. gr. 1.5; not decomposed on boiling the solution.  | Insoluble in alkalis.  | ... ..  | ... ..  | ... ..  | With acetate of lead, alcoholic solution gives no precipitate.   |  |   |
| Purpurin<br>$C_{14}H_8O_6$             | Crystallises in small orange-coloured or red needles.  | When heated carefully, it is volatilised without much residue, giving a sublimate of shining scales and needles.                                 | Slightly soluble in boiling water with a pink colour.   | Soluble in boiling alcohol and crystallises out on cooling.  | ... ..   | ... ..                                | Dissolved, not decomposed on boiling the solution.   | ... ..  | Decomposed by boiling dilute nitric acid, more easily than alizarin.   | Soluble in alkalis with bright purplish-red colour; solutions in caustic fixed alkalis lose their colour by the action of oxygen.  | Ammoniacal solution gives with chlorides of calcium and barium, purple precipitates.  | Soluble in boiling alum-liquor with a pink colour, not separating on cooling, but precipitated by hydrochloric acid.                          | ... ..  | With acetate of lead, alcoholic solution gives a purple precipitate, not changed on standing, which dissolves on boiling with excess of acetate of lead, giving a purple solution. |  |   |



PAID  
JUL 18 1878  
SPARKS

PAID  
JUL 18 1878  
SPARKS





# APPENDIX.



## TABLES

FOR DISTINGUISHING THE DIFFERENT

## COLOURING MATTERS

FIXED ON TISSUES BY PRINTING OR

DYEING.

| <i>Name of the colouring matter.</i>                    | <i>Combustion of the coloured fibre on platinum foil.</i>  | <i>Immersion in dilute hydrochloric acid.</i>               | <i>Immersion in dilute soda solution.</i>   |
|---|--|---|---|
| Vat Indigo.   | Leaves a small quantity of colourless ash, which sometimes contains lime, and may also contain a little oxide of iron. | No action.  | No action.  |
| Indigo carmine, alkaline sulphindigotates, Saxony blue. | Leaves a small quantity of white ash sometimes containing tin.   | Loses a little of its colour.                               | Loses a little of its colour; the solution, and sometimes the edges of the fabric becoming green.                                   |
| Prussian blue.  | Reddish ferruginous ash.   | Is not altered.   | Gradually becomes yellow. The solution supersaturated with HCl, becomes blue on the addition of a few drops of perchloride of iron. |
| Logwood blue.   | White residue, rarely greyish. The ash contains alumina, and occasionally a little oxide of copper.                    | Becomes red, as does also the liquid.                       | A little deeper in shade; pure blue.  |
| Aniline blue.   | Little ash, and no trace of any mordant with wool or silk.   | No alteration takes place.                                  | The dark shades become quickly violet, the lighter ones flesh-coloured.   |
| Ultramarine.  | Blue ashes.  | Is decolorised with disengagement of sulphuretted hydrogen. | No alteration.  |

| <i>Immersion in a solution of chloride of lime.</i>                              | <i>Immersion in a solution of permanganate of potash to which a little sulphuric acid has been added.</i> | <i>Remarks.</i>  |
|--|---|--|
| Bleaches slowly.   | Quickly becomes decolorised.  | This colouring matter may be met with on woollen, cotton, flaxen, and hempen fibres, but not upon silk. Nitric acid produces a pale yellow coloration. If the coloured fibre be placed in a capsule covered with a watch glass, and heat be cautiously applied, violet vapours having the characteristic odour of indigotin will soon make their appearance, and condense on the cool part of the watch glass.   |
| Bleaches slowly.   | Is slightly less changed than vat indigo.   | May be found on all fibres. After treating with nitric acid, sulphuric acid may easily be detected in the solution. The indigo cannot be separated by sublimation. Moistened with protochloride of tin, it becomes green, and afterwards yellow. Vat indigo resists the actions of these reagents a little better.   |
| No alteration takes place.   | Dirty green.  | Is met with upon silk, wool, and cotton fibre; becomes decolorised in presence of soap; fades in the light. Is not attacked by weak acids. Protochloride of tin and dilute hydrochloric acid produce no change.  |
| Is decomposed.   | The dark shades become brown, the light ones yellow.  | Alone, it is of a dull, dark, and dirty tint; but it is often associated with indigo on woollen and cotton fabrics; and if used to top the indigo colour, it is dissolved by hydrochloric acid, whilst the indigo is not affected.   |
| The colour is slowly destroyed; more rapidly upon cotton than upon wool or silk. | Slowly decolorised.   | Most frequently met with on silk and wool; and also on cotton and linen, on which it is fixed by albumen or sumach. Nitric acid gives a dark blue coloration at first, which afterwards becomes yellowish-blue. Under the influence of protochloride of tin and hydrochloric acid it suffers but little change; sometimes it becomes greenish, but recovers its colour when brought in contact with water. It behaves in a similar manner with concentrated hydrochloric acid. |
| .....  | .....   | Is only employed for printing; it is generally fixed with white of egg, consequently, on burning the tissue, even if it be cotton, products are formed similar to those obtained when nitrogenous bodies are burnt (smell of burnt horn, ammonia reaction).  |



| <i>Name of the colouring matter.</i> | <i>Combustion of the coloured fibre on a piece of platinum.</i>                          | <i>Boiling in water containing <math>\frac{1}{2}</math> per cent. of soap.</i> | <i>Immersion in dilute nitric acid.</i>                                    |
|--------------------------------------|--|--|--|
| Quercitron bark.                     | The ash contains alumina.  | The water becomes coloured, but the colour of the cloth is not much altered.   | Becomes brown.   |
| Persian berries.                     | The ash contains alumina, or if the coloration is more orange, tin is present.           | Behaves like the preceding.  | As the preceding.  |
| Old fustic.                          | The ash contains alumina.  | Almost decolorised.  | As the preceding.  |
| Weld.                                | The ash contains alumina, and sometimes, although rarely, tin.                           | Only slightly altered.   | Little changed.  |
| Barberry root.                       | Is not used with mordants.   | Little changed.  | Red-brown, as is also the liquid.  |
| Turmeric.                            | Generally used without mordants.   | Rapidly becomes brown, but recovers its colour by the action of acids.         | Little changed.  |
| Annatto.                             | Used without mordants.   | Takes a darker shade.  | At first reddish-brown, then yellowish-green, and lastly becomes bleached. |
| Picric acid.                         | Used without mordants.   | Loses its yellow colour.   | Little alteration.   |
| Chrome yellow and chrome orange.     | Lead will be found in the ash.   | Becomes more orange.   | Decolorises.   |
| Ochre.                               | Reddish - brown ash, containing oxide of iron.   | Generally more brilliant, otherwise no change.                                 | Is destroyed immediately.  |
| Orpiment.                            | The vapours arising from the burning cloth have the smell of sulphurous acid and garlic. | Little change.   | Little change.   |

| <i>Treating in a hot mixture of 100 c.c nitric acid, sp. gr. 1.5, 6 vols. water and 40 vols. of alcohol. To the extract a few drops of acetate of lead solution are added.</i> | <i>Immersion in caustic ammonia.</i>  | <i>Remarks.</i>   |
|--|---|---|
| The acid extract is yellow. The voluminous precipitate pale yellow.  | Whilst wet it appears brown, but when dry is found to have changed very little. | The reactions of this and the two following colouring matters are very similar, the chemical nature of the colouring principle being analogous.   |
| The same as the preceding.   | The tone changes a little; colour slightly dissolved.                           | Persian berries are only used for printing, and not for dyeing. They are employed with a salt of alumina as a mordant for yellow, and a salt of tin for orange; the latter, however, is not a good tint.                    |
| As the preceding.  | Becomes coloured orange; the liquid becomes coloured also.                      | If the extract obtained by nitric acid and alcohol be evaporated, and a little concentrated sulphuric acid then added, a red coloration is produced, which is more intense upon wool than on cotton fibre (rufimoric acid). |
| Like the preceding.  | Slightly altered.   | This colouring matter is employed for every sort of fibre.  |
| No visible precipitation.  | Red-brown.  | Is only employed for dyeing silk.   |
| Dense orange-brown precipitate.  | Reddish-brown coloration.   | Is seldom employed alone; generally with other yellow pigments.   |
| No visible precipitate.  | Little alteration.  | Is not a pure yellow, but generally orange.   |
| No precipitate.  | Clear yellow; loses a little of its colour.                                     | Only dyes silk and wool; is generally met with only on the former. A solution of cyanide of potassium colours it red-brown; which reaction must not be confounded with that of the alkalis with turmeric.                   |
| .....  | The colour is partially removed, and becomes orange-yellow.                     |   |
| Is destroyed, the solution contains iron.  | No alteration.  | If a little hydrochloric acid be first added, and then some potassium ferrocyanide, a blue coloration is produced.  |
| .....  | Greater part dissolves.   | Very little employed.   |

| <i>Name of the colouring matter.</i> | <i>Combustion on a piece of platinum foil.</i>  | <i>Boiling in water containing <math>\frac{1}{2}</math> per cent. of soap.</i> | <i>Moistened with a solution of carbonate of soda.</i>                                |
|--------------------------------------|---|--|---|
| Cochineal.                           | The ashes contain alumina, or oxide of tin, or both these bases.  | The colour is but little changed, the liquid is a faint violet colour.         | The liquid is coloured a little without perceptibly altering the colour of the fibre. |
| Brazil wood.                         | Ashes generally contain alumina.  | The colour disappears; the liquid becomes red-brown.                           | The liquid quickly becomes coloured, the fibre remains red.                           |
| Madder reds.                         | Alumina will be found in the ashes.   | The colour becomes brighter.   | A little colour is removed, but the shade remains unchanged.                          |
| Safflower.                           | The ash does not contain any mordant.   | Quickly and completely decolorised.  | The fibre becomes flesh-coloured, and acquires a yellowish tint.                      |
| Murexide.                            | The fibre contains a little oxide of lead or mercury, (the latter is detected by heating a piece of the cloth in a tube). | Is moderately permanent.   | Becomes lilac-coloured; a little of the colour is removed.                            |
| Aniline reds.                        | The ash generally does not contain a mordant.   | Become more brilliant upon wool at first, and is then rapidly discolored.      | Preserves its colour well.  |



| <i>Immersion in caustic ammonia.</i>   | <i>Moistened with a solution of citric acid.</i>                         | <i>Moistened with a solution of equal parts of tin salt, hydrochloric acid, and water.</i>  | <i>Remarks.</i>   |
|--|--|---|---|
| A little of the colour is removed; the liquid becomes violet.  | Becomes yellow, and the colour cannot be completely restored by ammonia. | A little of the colour is removed; the fibre becomes yellow.  | On silk, wool, and cotton.  |
| Much colour is removed. Cotton is almost decolorised.  | Reddish-yellow; the colour is restored by ammonia.                       | The tissue becomes tinted yellow.   | On silk and cotton, rarely on wool. The colour fades in presence of soap.   |
| On wool and silk rather brown; but Turkey reds and alumina reds on calico undergo but slight change.                 | Unaltered.   | Almost unaltered; only a little of the colour is removed.   | Resists the action of all reagents better than other reds.  |
| The fibres and the liquid become reddish-yellow.   | Is permanent.  | It assumes a fine straw-yellow colour   | Is not met with upon wool; most generally upon silk, sometimes also on cotton.                                    |
| Retains its colour well.   | Bleaches quickly.  | Quickly becomes grey.   | It was met with often on dyed and printed cotton goods, but more frequently upon wool; it is now rarely employed. |
| Becomes palerose-red, then colourless. When the ammonia absorbed by the fibre has evaporated the colour is restored. | Stands well.   | Is decolorised gradually in places which are only slightly touched by the reagent; the fibre becomes blue before being decolorised. | On wool and silk.   |

---

*The ashes contain neither iron nor lead.*

---

In this group may be classed: 1st, Indigo-blue and vegetable yellow; 2nd, Logwood blue and a vegetable yellow; 3rd, Lo-kao; 4th, Aniline green; 5th, Aniline blue and picric acid, or vegetable yellow; 6th, (Scheeles green or arsenite of copper); 7th, Oxide of chromium.

1a. Vat indigo may be recognised by heating a piece of the cloth in a porcelain capsule; the indigo volatilises (see blue colouring matters).

1b. Carmine of indigo does not give this reaction. They both become greenish-yellow when moistened with tin salt and hydrochloric acid. Nitric acid decomposes both, leaving the yellow colour but slightly altered. The ashes of both contain alumina, in consequence of salts of that base being employed as mordants for the yellow colour.

2. Logwood blue and vegetable yellow. Hydrochloric acid produces a yellowish-red coloration; the liquid becomes yellowish, but blue or green on the addition of an alkali. Alumina is contained in the ashes.

No satisfactory method is yet known for determining the yellow vegetable colouring matter which is mixed with the blue colour.

3. Chinese green (lo-kao). No mordant base in the ash, but sometimes a little lime. Does not change in presence of acids or alkalis if they are not too concentrated. It is only used for dyeing silk, but is now rarely found.

4. Aniline green. No mordant base in the ash. Moistened with hydrochloric acid (concentrated) it immediately becomes yellow, or even colourless. The colour is, however, again restored when water is added.

5. Aniline blue, and vegetable yellow or picric acid. The blue is not altered by chloride of tin and hydrochloric acid. This mixture is rarely met with.

6. Scheele's green. Fused with carbonate of soda it gives in the reducing flame of the blowpipe, a globule of metallic copper. Heated in a small open glass tube, it gives a deposit of arsenious acid, and a smell of garlic.

7. Oxide of chromium. Fused with a little potassium nitrate, it gives a yellow soluble mass, which, mixed with a little acetic acid and a solution of acetate of lead, gives a yellow precipitate. It is only employed for printing fibres.

---

| <i>The ashes contain lead but no iron.</i>   | <i>The ashes contain iron but no lead.</i>   | <i>The ashes contain iron and lead.</i>   |
|--|--|---|
| <p>8. Chrome yellow and indigo blue.</p> <p>A piece of the cloth soaked in soda-ley becomes more blue, and the solution contains a little chromate of potash. Chloride of lime leaves the yellow, but destroys the blue. The ashes fuse into an incandescent bead of a brownish yellow color, which, if mixed with carbonate of soda and again fused, leaves a globule of metallic lead.</p> | <p>9. Prussian blue and vegetable yellow. Placed in caustic soda solution, the piece becomes brown-yellow: if a little hydrochloric acid be added to the filtered liquid and then perchloride of iron, a blue or greenish-blue precipitate will be produced.</p> | <p>10. Prussian blue and chromate of lead. The lead may be detected as given in No. 8 by reduction to the metallic state. The chromic acid remains in combination with the soda, so that the product of the fusion, dissolved in water, gives with acetic acid and acetate of lead, a yellow precipitate.</p> |



| <i>Name of the colour.</i>                               | <i>Moistened with concentrated hydrochloric acid.</i>   | <i>Moistened with a mixture of equal parts of chloride of tin, hydrochloric acid, and water.</i> |
|--|---|--|
| Perkin's aniline purple (prepared with chromic acid).    | Becomes blue, but recovers its original colour when immersed in water.  | Almost unchanged.  |
| Aniline purple obtained with magenta and aniline.        | Becomes green; the liquid a little reddish. Placed in water it takes its original colour.                           | Same reaction as that with hydrochloric acid.  |
| Hofmann's aniline violet, obtained with iodide of ethyl. | Becomes yellow, sometimes taking a green coloration previously; its colour is also restored by placing it in water. | Ditto.   |
| Madder purples.  | Becomes red-brown. Water does not restore its colour.   | Becomes of a slightly reddish-brown. The liquid takes up very little colour.                     |
| Alkanet.   | Becomes more lilac-colored, but none of the colour is removed.  | Undergoes but little alteration, which is less marked as the colour is more blue.                |
| Orchil.  | Becomes clearer; rather brick-red.  | Is immediately and completely decolorised.   |
| Logwood purple.  | Becomes red; much of the colour is removed, and the solution becomes red.   | Fades much to violet-red.  |

| <i>Immersion in a solution of ammonia.</i>                                 | <i>Immersion in a solution of carbonate of potash or soda.</i>   | <i>Remarks.</i>   |
|--|--|---|
| Loses brilliancy.  | Becomes blue.  | For wool and silk, no mordant base in the ash. For cotton sometimes alumina.  |
| Ditto.   | Unchanged.   | Same as the preceding colour.   |
| Ditto.   | Ditto.   | Ditto.  |
| Ditto.   | Rather more violet, but none of the colour is removed.   | The ash contains iron. Almost exclusively employed for cotton goods.  |
| Ditto.   | Little changed, none of the colour is removed.   | On silk and cotton. No mordant base in the ash.   |
| Becomes violet-blue.   | At the ordinary temperature the colour is rather bluish. If warmed the solution also becomes coloured violet-blue. | No mordant base. Is found on wool, silk, or cotton, often with a blue or brown-red shade, produced by indigo or cochineal. These colours do not generally affect the reactions. |
| The colour fades to violet, as dark as that produced by the acid solution. | Same as with ammonia.  | The ash contains oxide of tin.  |

| <i>Name of the colour.</i>   | <i>Moistened with concentrated hydrochloric acid.</i>   | <i>Moistened with a solution of equal parts of tin salt, hydrochloric acid, and water.</i> |
|--|---|--|
| Madder.  | Becomes red or orange-colored. Ammonia restores the original colour.                                    | Same reaction as with hydrochloric acid.   |
| Catechu.   | Stands well; if other colouring matters have been employed with it, it only becomes of a lighter shade. | Same reaction as with hydrochloric acid.   |
| Browns produced with various woods (logwood, and a red dyewood).   | Destroyed, and violet coloration produced.  | Destroyed, and violet coloration produced.   |
| Manganese.   | Little alteration.  | Is slowly decomposed.  |
| <p>Brown produced by the employment of blue, yellow, and red upon wool.</p> <p><i>a.</i>—Ground or bottom of indigo.</p> <p><i>b.</i>—Ground or bottom of Prussian blue.</p> | <p>Is not altered, the blue resists the action well.</p> <p>.....</p>                                   | <p>Becomes green. Not much altered. The blue resists the action well.</p>                  |

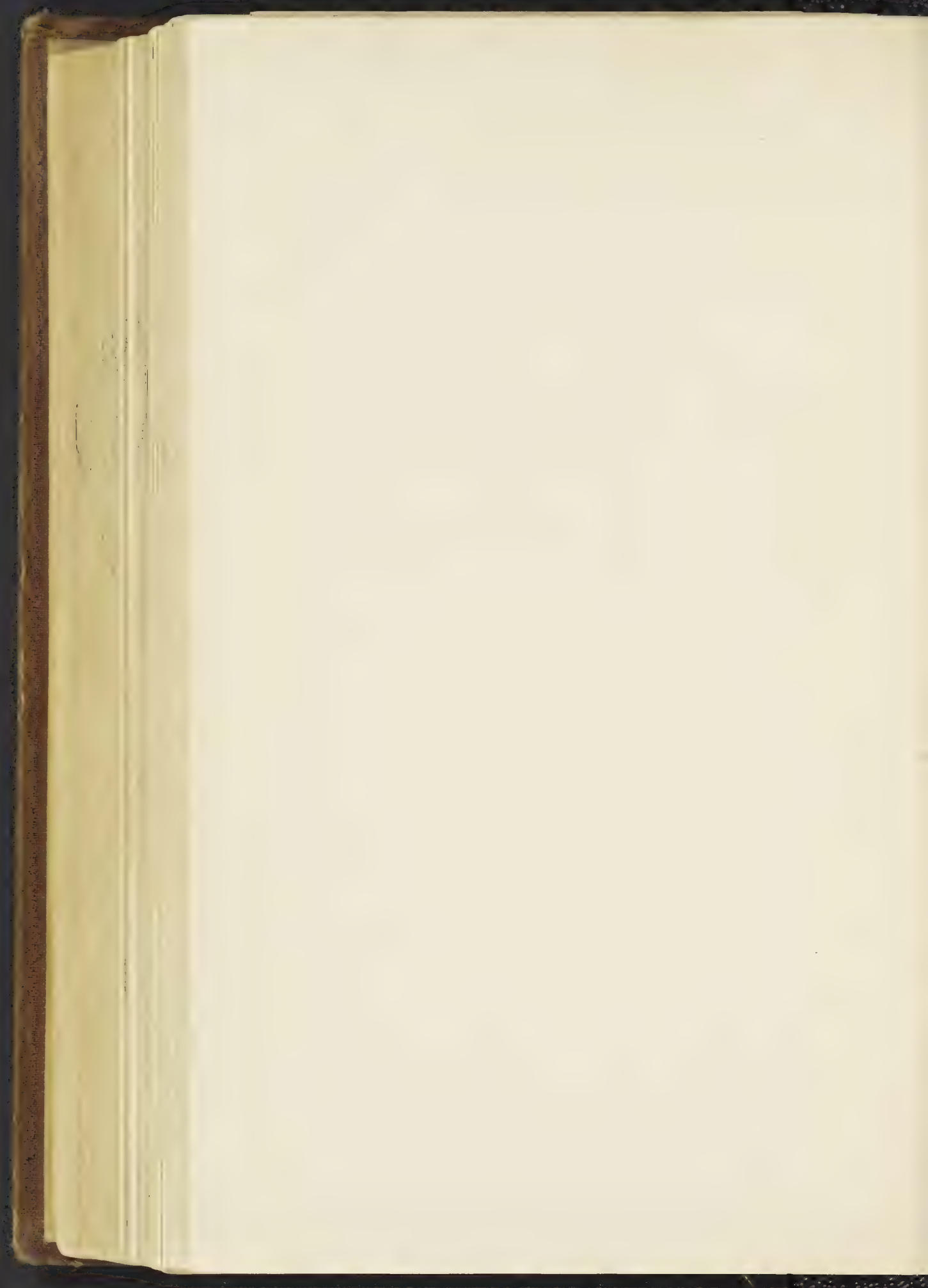


| <i>Burning on a piece of platinum foil.</i>  | <i>Remarks.</i>   |
|--|---|
| The ash contains oxide of iron and alumina.  | Only employed for colouring cotton, linen, and hempen fibres.   |
| Ashes greenish-grey. Heated with borax before the blow-pipe it gives a green glass.    | This colour is rarely produced by the employment of catechu and bichromate of potash only; but logwood, carmine of indigo, orchil, or turmeric are generally employed at the same time, to produce various shades. These substances render its detection difficult; the chromium in the ash, and a certain resistance to the action of acids, are characteristic. |
| The ash contains alumina and sometimes also oxide of iron.                             | Besides these two woods, others are employed for making brown. The reactions are then less certain.   |
| The ash contains manganese, which gives a red coloration to a bead of borax.           | Now little employed. This colouring matter gives a good shade. Is sometimes employed with indigo to produce a deep blue.  |
| The ash contains alumina; and when the ground is of Prussian blue, also oxide of iron. | It is often difficult to identify this in consequence of the simultaneous presence of different substances.   |

| <i>Name of the colour.</i>                  | <i>Burning upon a piece of platinum foil.</i> | <i>Immersion in hydrochloric acid.</i>          |
|---|---|---|
| Logwood (iron mordant).                     | The ash contains oxide of iron.               | Is decolorised, giving a cherry-red colour.     |
| Tannin.                                     | Ash contains oxide of iron.                   | White spots, becoming rust-colored by ammonia.  |
| Chrome black.                               | The ash contains oxide of chromium.           | Becomes reddish.                                |
| Madder black.                               | The ash contains oxide of iron and alumina.   | Becomes red; the colour is restored by ammonia. |
| Black, with bottom or ground of vat indigo. | Ash contains a little iron.                   | Becomes blue.                                   |
| Aniline black.                              | Very light ash.                               | After some time a green shade appears.          |

| <i>Immersion in a mixture of equal parts of chloride of tin, water, and hydrochloric acid.</i>     | <i>Remarks.</i>  |
|--|--|
| Violet, fades quickly.   |  |
| Same reaction as with hydrochloric acid.   |  |
| Violet, a rather large quantity of the colour is removed.  |  |
| Same reaction as with hydrochloric acid.   | Is only employed for printing.   |
| Becomes greenish-blue.   | It is the beautiful black which is formed upon wool. If care be first taken to remove by dilute acid any galate of iron or logwood, the indigo may then be recognised as directed in the table for blue colouring matters. |
| Becomes rapidly green, then greenish-grey; the colour is not restored by water, but is by ammonia. | Is almost exclusively employed for printing on cotton.   |





# INDEX.

|                               | Page.    |
|-------------------------------|----------|
| <i>ABIES canadensis</i> ..... | 328      |
| <i>Acacia bambolah</i> .....  | 327      |
| „ <i>catechu</i> .....        | 330      |
| „ <i>nilotica</i> .....       | 327      |
| Acetophenone .....            | 169      |
| Acetylramnetin .....          | 273      |
| Acid, aloeresic .....         | 282      |
| „ aloeretic .....             | 282      |
| „ aloetic .....               | 282      |
| „ anchusic .....              | 134      |
| „ anthraflavic .....          | 44       |
| „ anthranilic .....           | 167      |
| „ $\beta$ -usnic .....        | 245      |
| „ bezoardic .....             | 321      |
| „ bromisatic .....            | 166      |
| „ brunolic .....              | 428      |
| „ cachoutannic .....          | 333      |
| „ carbazotic (picric) .....   | 452      |
| „ carminic .....              | 209      |
| „ carthamic .....             | 136, 137 |
| „ catechuic .....             | 334      |
| „ catechutannic .....         | 333      |
| „ chloranilic .....           | 166      |
| „ chloroxynaphthalic .....    | 474      |
| „ chrysammic .....            | 283      |
| „ chrysammidic .....          | 284      |
| „ chrysanilic .....           | 167      |
| „ chrysophanic .....          | 296, 298 |
| „ chrysinic .....             | 296      |
| „ cladonic .....              | 245      |
| „ dibromisatic .....          | 166      |
| „ digallic .....              | 313      |
| „ ellagic .....               | 321      |
| „ erythric .....              | 239      |
| „ euxanthic .....             | 297      |
| „ evernic .....               | 245      |
| „ everninic .....             | 245      |
| „ gallic .....                | 313      |
| „ gallotannic .....           | 311      |
| „ hydrindic .....             | 170      |
| „ hyposulphindigotic .....    | 177      |
| „ indigotic .....             | 162      |
| „ isamic .....                | 161      |
| „ isatic .....                | 160      |
| „ isopurpuric .....           | 456      |

HH

|  | Page.         |
|--|---------------|
| Acid, iso-uvitic .....                 | 295           |
| „ japonic .....                        | 335           |
| „ lecanoric .....                      | 240           |
| „ meta-amidobenzoic .....              | 167           |
| „ metagallic .....                     | 312, 317      |
| „ mimotannic .....                     | 333           |
| „ moric .....                          | 264, 266      |
| „ morintannic .....                    | 264           |
| „ naphthalene-sulphonic ..             | 471           |
| „ naphthylpurpuric .....               | 473           |
| „ nitrocinnamic .....                  | 172           |
| „ nitrococcusic .....                  | 213           |
| „ nitrosalicylic .....                 | 162           |
| „ nitroxynaphthalic .....              | 475           |
| „ orsellesic .....                     | 246           |
| „ orsellic .....                       | 241           |
| „ orsellinic .....                     | 246           |
| „ oxalic, from garancin washings ..... | 86            |
| „ oxynaphthalic .....                  | 56            |
| „ oxyphenic .....                      | 336           |
| „ oxytoluic .....                      | 360           |
| „ paracoumaric .....                   | 282           |
| „ paraoxybenzoic .....                 | 282           |
| „ parellic .....                       | 247           |
| „ phenylcarbamic .....                 | 167           |
| „ picramic .....                       | 456           |
| „ picric .....                         | 163, 452      |
| „ picrocyamic .....                    | 456           |
| „ protocatechuic ..                    | 258, 264, 335 |
| „ pyrocatechuic .....                  | 336           |
| „ pyrogallic .....                     | 316           |
| „ quercetic .....                      | 257, 258      |
| „ quercimeric .....                    | 258           |
| „ quercitannic .....                   | 255, 328      |
| „ regianic .....                       | 329           |
| „ rhotic .....                         | 329           |
| „ rocellic .....                       | 247           |
| „ rosolic .....                        | 458           |
| „ ruberythric .....                    | 35            |
| „ rubiacic .....                       | 30, 33        |
| „ rubianic .....                       | 36            |
| „ rubinic .....                        | 335           |
| „ rufigallic .....                     | 315           |
| „ rufimoric .....                      | 265           |

|                                       | Page.      |                                  | Page.    |
|---------------------------------------|------------|----------------------------------|----------|
| Acid, rufitannic .....                | 313        | Alizarin, oxidation of .....     | 41       |
| „ salicylic .....                     | 163        | „ yellow .....                   | 93       |
| „ santalic .....                      | 129        | Alizarinamide .....              | 42       |
| „ styphnic .....                      | 123        | Alizarinimide .....              | 43       |
| „ sulphindigotic .....                | 176        | Alkalis, action of on indican .. | 155      |
| „ sulphoflavic .....                  | 181        | Alkanet .....                    | 134      |
| „ sulphonaphthalic .....              | 471        | Alloxan .....                    | 226      |
| „ sulphopurpuric .....                | 175, 181   | Aloeresic acid .....             | 282      |
| „ sulphorufic .....                   | 181        | Aloeretic „ .....                | 282      |
| „ sulphoviridic .....                 | 180        | Aloeretin .....                  | 282      |
| „ sulphurous, bleaching ac-           |            | Aloes .....                      | 278      |
| tion of .....                         | 16         | „ Barbadoes .....                | 279      |
| „ taiguic .....                       | 300        | „ Bombay .....                   | 279      |
| „ tannic .....                        | 311        | „ Cape .....                     | 279      |
| „ tannoxylic .....                    | 313        | „ colours yielded by .....       | 284      |
| „ tribromomoric .....                 | 266        | „ hepatic .....                  | 279      |
| „ triphenylosaniline-sulpho-          |            | „ liver .....                    | 279      |
| nic .....                             | 407        | „ Natal .....                    | 279      |
| „ uric .....                          | 225        | „ Socotrine .....                | 279      |
| „ usnic .....                         | 244        | „ Zanzibar .....                 | 279      |
| „ vulpic .....                        | 296, 297   | Aloetic acid .....               | 282      |
| „ xylochloric .....                   | 309        | Aloin .....                      | 280      |
| Acids, action of on indican .....     | 150        | Amidoalizarin .....              | 42       |
| „ indigosulphonic .....               | 175        | Amidodinitrophenol .....         | 456      |
| Action of acids on indican .....      | 150        | Amidodiphenylimide .....         | 429      |
| „ alkalis on indican .....            | 155        | Ammonia, hæmatæate of .....      | 115      |
| „ chlorine on colouring               |            | Ammoniacal cochineal .....       | 218      |
| matters. ....                         | 13         | Ammonium lokaetin .....          | 304      |
| „ „ indigo ...                        | 164        | Amylic orsellinate .....         | 242      |
| „ electricity on flowers..            | 10         | Amylorcin .....                  | 238      |
| „ light on guaiacum ...               | 6          | Analysis of white light .....    | 2        |
| „ heat on colouring mat-              |            | <i>Anchusa tinctoria</i> .....   | 134      |
| ters .....                            | 11         | Anchusic acid .....              | 134      |
| Adrianople red .....                  | 64         | Anchusin .....                   | 134      |
| Adulteration of aniline yellow ...    | 431        | Aniline .....                    | 356      |
| „ annatto .....                       | 289        | Aniline black, aniline for ..... | 445      |
| „ catechu .....                       | 333        | „ composition of ...             | 442      |
| „ cochineal .....                     | 214        | „ Dullo's .....                  | 439      |
| „ madder .....                        | 104        | „ Jarossen and Mül-              |          |
| „ magenta .....                       | 379        | ler's .....                      | 441      |
| Adulterations, detection of .....     | 348        | „ Koechlin's .....               | 438      |
| Ageing .....                          | 77         | „ Lauth's .....                  | 437, 439 |
| Al root .....                         | 111        | „ Lightfoot's .....              | 436      |
| Alcohol from madder .....             | 89         | „ „ experi-                      |          |
| Aldehyde green .....                  | 414        | ments on .....                   | 443      |
| „ violet .....                        | 400        | „ nature of .....                | 442      |
| Aleppo galls .....                    | 322        | „ Persoz' .....                  | 447      |
| Alizaric extract .....                | 93         | „ Sacc's .....                   | 438      |
| Alizarin, 25, 30, 32, 35, 38, 93, 111 |            | „ Schlumberger's ...             | 441      |
| „ anthracene, from .....              | 41         | „ Spirk's .....                  | 440      |
| „ artificial .....                    | 44, 48, 54 | Aniline blues .....              | 402      |
| „ „ Graebe's patent                   | 50         | „ „ dyeing with .....            | 411      |
| „ „ printing with ...                 | 100        | „ browns .....                   | 432      |
| „ commercial .....                    | 87         | „ commercial .....               | 362      |
| „ from anthracene .....               | 44         | „ discovery of .....             | 352      |
| „ green .....                         | 93         | „ for aniline black .....        | 448      |
| „ hydrate .....                       | 39         | „ from coal-tar .....            | 353      |
| „ hydride of .....                    | 40         | „ from indigo .....              | 169, 353 |
| „ optical characters of ...           | 62         | „ greens .....                   | 414      |



|                                   | Page.      |                                    | Page.    |
|-----------------------------------|------------|------------------------------------|----------|
| Aniline grey, Laüber's .....      | 448        | Berlin lake .....                  | 128      |
| „ heavy.....                      | 363        | $\beta$ -erythrin .....            | 247      |
| „ light .....                     | 363        | $\beta$ -orcin .....               | 245, 247 |
| „ manufacture of.....             | 356        | $\beta$ -usnic acid .....          | 245      |
| „ maroons .....                   | 432        | Bezoardic acid .....               | 321      |
| „ violets .....                   | 384        | <i>Bigonia chica</i> .....         | 291      |
| „ yellow, adulteration of..       | 431        | Binitroanthraquinone .....         | 50       |
| „ yellows .....                   | 425        | <i>Bixia orellana</i> .....        | 288      |
| Animal charcoal.....              | 14         | Bixin .....                        | 290      |
| Annatto .....                     | 288        | Black, aniline.....                | 435      |
| „ adulteration of .....           | 289        | „ logwood .....                    | 120      |
| „ composition of .....            | 288        | „ mordant .....                    | 75       |
| „ reactions of .....              | 289        | Bladder green.....                 | 305      |
| „ uses of .....                   | 291        | Blanco .....                       | 208      |
| Anthracene .....                  | 46         | Bleaching action of sulphurous     |          |
| „ alizarin from.....              | 44         | acid .....                         | 16       |
| „ discovery of .....              | 44         | Bleu de Lyon.....                  | 402      |
| „ from alizarin.....              | 41         | „ „ manufacture of.....            | 403      |
| „ orange .....                    | 55         | „ Mulhouse.....                    | 402      |
| „ purification of .....           | 46         | „ Nemours .....                    | 131      |
| „ properties of.....              | 47         | „ Paris.....                       | 402      |
| Anthraflavic acid .....           | 44         | Bleu lumière .....                 | 404      |
| Anthranilic acid .....            | 167        | Blue and violet, Bardy's process   |          |
| Anthrapurpurin .....              | 45         | for .....                          | 405      |
| Anthraquinone .....               | 49         | „ azodiphenyl .....                | 411      |
| Apparatus for evaporation .....   | 147        | „ diphenylamine .....              | 408, 410 |
| <i>Areca catechu</i> .....        | 330        | „ Nicholson's .....                | 407      |
| Artificial alizarin .....         | 44, 48, 54 | „ night .....                      | 404      |
| „ „ Graebe's patent .....         | 50         | „ Runge's.....                     | 388      |
| „ „ printing with... ..           | 100        | „ Saxony .....                     | 178      |
| Assistant liquor, purple.....     | 73         | „ toluidine .....                  | 408      |
| Aurin .....                       | 466        | Blues, aniline .....               | 402      |
| Azodinaphthylamine .....          | 477        | Bombay catechu.....                | 331      |
| Azodiphenyl blue .....            | 411        | Brazil wood .....                  | 121      |
| Azodiphenylamine .....            | 429        | „ dyeing with.....                 | 126      |
| Azolitmin .....                   | 248        | „ extract.....                     | 125      |
| Azoresorcin derivatives.....      | 250        | „ „ reactions of... ..             | 125      |
| Azulín .....                      | 464        | „ rose colour .....                | 127      |
| BABLAH .....                      | 327        | Brazilein .....                    | 124      |
| Babool.....                       | 327        | Brazilin .....                     | 123      |
| Bahia wood .....                  | 122        | Britannia violet .....             | 400      |
| <i>Baphia nitida</i> .....        | 128        | Bromalizarin .....                 | 43       |
| Baraniline .....                  | 363        | Bromaloin .....                    | 281      |
| Barbadoes aloes .....             | 279        | Bromisatic acid .....              | 166      |
| Barbaloin .....                   | 280        | Bromisatin .....                   | 166      |
| Barberry root .....               | 292        | Bromobenzene .....                 | 359      |
| Bardy's process for blue & violet | 405        | Bromorcins .....                   | 236      |
| Barwood .....                     | 128, 131   | Brou-de-noix .....                 | 329      |
| „ reactions of... ..              | 132        | Brown, Girard and De Laire's...    | 432      |
| Bengal catechu .....              | 331        | „ Jacobsen's.....                  | 433      |
| Benzene .....                     | 353        | „ Koechlin's.....                  | 433      |
| Benzidam .....                    | 352        | „ Sieberg's .....                  | 434      |
| Benzoylalizarin .....             | 43         | „ Wise's .....                     | 434      |
| Benzyl chloride .....             | 399        | Browns, aniline .....              | 432      |
| Benzyllic violets .....           | 399        | Brunolic acid .....                | 458      |
| Berberine.....                    | 293        | <i>Butea frondosa</i> .....        | 330      |
| <i>Berberis aristata</i> .....    | 293        |                                    |          |
| „ <i>vulgaris</i> .....           | 292        | <i>CÆSALPINIA braziliensis</i> ... | 121      |

|                                   | Page.    |                                      | Page.    |
|-----------------------------------|----------|--------------------------------------|----------|
| <i>Casalpinia christa</i> .....   | 121      | Chlorine, action of on colouring     |          |
| „ <i>coriaria</i> .....           | 328      | „       „       matters.             | 13       |
| „ <i>echinata</i> .....           | 122      | „       „       indigo               | 164      |
| „ <i>sappan</i> .....             | 122      | Chlorisatin .....                    | 165      |
| Cachoutannic acid .....           | 333      | Chlorogenin .....                    | 28, 29   |
| Caliatour wood .....              | 133      | Chlorophyll .....                    | 305      |
| Calico printing .....             | 72       | „       composition of .....         | 308      |
| California wood .....             | 122      | „       printing with .....          | 309      |
| Calumbo root .....                | 293      | Chlororcins .....                    | 236      |
| Campeachy wood .....              | 113      | Chlorotoluene .....                  | 399      |
| Campo Bello yellow .....          | 469      | Chloroxynaphthalic acid .....        | 474      |
| Camwood .....                     | 128      | Chloroxynaphthaquinone .....         | 474      |
| Cape aloes .....                  | 279      | Chocolate chromium .....             | 99       |
| Carajara .....                    | 291      | „       mordant, dark .....          | 75       |
| Carbazotic acid .....             | 452      | „       „       light .....          | 75       |
| Carmin de pourpre .....           | 227      | Chromium chocolate .....             | 99       |
| Carminamide .....                 | 218      | Chrysammic acid .....                | 283      |
| Carminaphtha .....                | 475      | Chrysammidic acid .....              | 284      |
| Carmine .....                     | 209, 219 | Chrysanic acid .....                 | 167      |
| „   indigo .....                  | 178, 179 | Chrysanine .....                     | 425      |
| „   lakes .....                   | 218      | Chrsinic acid .....                  | 296      |
| „   red .....                     | 211      | Chrysophanic acid .....              | 296      |
| „   sorgho .....                  | 134      | Chrysopicrin .....                   | 296      |
| Carminic acid .....               | 209, 212 | Chrysorhamnin .....                  | 271, 272 |
| Carotin .....                     | 301      | Chrysotoluidine .....                | 367, 426 |
| Carthamic acid .....              | 136, 137 | <i>Cladonia rangiferina</i> .....    | 245      |
| Carthamin .....                   | 136, 137 | Cladonic acid .....                  | 245      |
| <i>Carthamus tinctorius</i> ..... | 136      | Clearing madder dyed goods ..        | 83       |
| Casthelaz grey .....              | 449      | „   Turkey red .....                 | 68       |
| Catechin .....                    | 334      | „   with hypochlorite of             |          |
| Catechu .....                     | 330      | soda .....                           | 84       |
| „   adulteration of .....         | 333      | Coal-tar, aniline from .....         | 353      |
| „   Bengal .....                  | 331      | „   colours .....                    | 350      |
| „   Bombay .....                  | 331      | „   constituents of .....            | 350      |
| „   brown .....                   | 337      | „   distillation of .....            | 352      |
| „   dyeing with .....             | 337      | „   naphtha .....                    | 352      |
| „   Gambier .....                 | 331      | Coccigranum .....                    | 220      |
| „   reactions of .....            | 332      | Coccinin .....                       | 212      |
| Catechuic acid .....              | 334      | <i>Cocculus palmatus</i> .....       | 293      |
| Catechuretin .....                | 335      | <i>Coccus cacti</i> .....            | 206      |
| Catechutannic acid .....          | 333      | „ <i>ilicis</i> .....                | 220      |
| Cerise .....                      | 382      | „ <i>lacca</i> or <i>ficus</i> ..... | 206      |
| <i>Cetraria vulpina</i> .....     | 296      | „ <i>Polonicus radicans</i> .....    | 206      |
| Chalk, use of in madder dye-      |          | Cochineal .....                      | 206, 207 |
| ing .....                         | 27, 81   | „   adulteration of .....            | 214      |
| Charbon de garance .....          | 25       | „   ammoniacal .....                 | 218      |
| Charcoal .....                    | 13       | „   dyeing with .....                | 216      |
| „   animal .....                  | 14       | „   history .....                    | 206      |
| Chayaver .....                    | 108, 110 | „   preparation of .....             | 208      |
| Chesnut bark .....                | 328      | „   reactions of .....               | 213      |
| Chica .....                       | 291      | „   testing .....                    | 215      |
| China blue .....                  | 203      | <i>Calocline polycarpa</i> .....     | 293      |
| Chinese galls .....               | 323      | Coerulein .....                      | 319      |
| „   green .....                   | 301      | Coerulin .....                       | 320      |
| „   sugar cane .....              | 133      | Cohen's vat (indigo) .....           | 199      |
| Chintz .....                      | 72       | Cold vat (indigo) .....              | 197      |
| Chloraloin .....                  | 281      | Colombo root .....                   | 293      |
| Chloranil .....                   | 166      | Colorometer .....                    | 342      |
| Chloranilic acid .....            | 166      | Colour, cause of .....               | 2        |



|                                      | Page.    |  | Page.    |
|--------------------------------------|----------|--|----------|
| Colour, recovery of waste            | 101, 102 | Dead oil                                     | 352      |
| Colour-giving principles             | 2        | Decomposition of rubian                      | 29       |
| Colouring matters                    | 2, 7     | Detection of adulteration                    | 348      |
| "    action of chlorine on           | 13       | "    purpurin                                | 63       |
| Colouring matters, action of heat on | 11       | Determination of tannin                      | 338      |
| Colouring matters of flowers         | 7        | Diacetylalizarin                             | 41       |
| "    nature of                       | 3        | Diamidonitrophenol                           | 456      |
| Colours                              | 1        | Diamylorcin                                  | 239      |
| "    coal-tar                        | 350      | Diazoamidobenzene                            | 429      |
| "    cresol                          | 469      | Diazoescorcin                                | 250      |
| "    effect of heat on               | 20       | Diazoesorufin                                | 250      |
| "    fast                            | 19       | Dibromindin                                  | 161      |
| "    loose                           | 19       | Dibromisatic acid                            | 166      |
| "    naphthalene                     | 470      | Dibromisatin                                 | 166      |
| "    obtained from aloes             | 284      | Dichlorisatin                                | 165      |
| "    on cloth, madder                | 107      | Dichlorisatyde                               | 166      |
| "    spectroscopic examination of    | 346      | Diethylorcin                                 | 239      |
| Columbo wood                         | 293      | Difference between garancin and madder style | 87       |
| Commercial alizarin                  | 87       | Digallic acid                                | 313      |
| "    aniline                         | 362      | Dimethyliodide of trimethylrosaniline        | 416, 421 |
| "    indigo                          | 189      | Dinitrobenzene                               | 356      |
| Comparison of dyestuffs              | 347      | Dinitrocresol                                | 469      |
| Composition of aniline black         | 442      | Dinitronaphthol                              | 471      |
| "    annatto                         | 288      | Dinitrotoluenes                              | 361      |
| "    chlorophyll                     | 308      | Dioxindol                                    | 170      |
| "    cochineal                       | 209      | Diphenylamine                                | 409      |
| "    gamboge                         | 295      | "    blue                                    | 408, 410 |
| "    madder                          | 24       | Diphenylrosaniline                           | 391      |
| "    safflower                       | 136      | Discovery of magenta                         | 364      |
| "    shell-lac                       | 224      | "    of mauve                                | 384      |
| "    stick-lac                       | 222      | Discharge process (indigo)                   | 201      |
| "    turmeric                        | 285      | Distillation of coal tar                     | 352      |
| Constituents of coal-tar             | 350      | Disulphisatyde                               | 161      |
| Corallin                             | 459      | Dividivi                                     | 328      |
| "    red                             | 462      | Dorothea violet                              | 398      |
| "    yellow                          | 466      | Dunging                                      | 78       |
| <i>Coriaria myrtifolia</i>           | 324      | Dutch yellow                                 | 275      |
| Cotton, dyeing with indigo           | 199      | Dyebeck                                      | 79       |
| Cresol colours                       | 469      | Dyeing cotton with indigo                    | 199      |
| Crocin                               | 292      | "    madder                                  | 81       |
| <i>Crocus sativus</i>                | 292      | "    power of garancin                       | 86       |
| <i>Croton tinctorium</i>             | 249      | "    Turkey red                              | 67       |
| Crystallin                           | 352      | "    with aniline blue                       | 411      |
| Crystallised green                   | 420      | "    "    brazil wood                        | 126      |
| Cudbear                              | 247      | "    "    catechu                            | 337      |
| <i>Curcuma longa</i>                 | 284      | "    "    cochineal                          | 216      |
| " <i>tinctoria</i>                   | 284      | "    "    indigo                             | 196      |
| Curcumin                             | 285      | "    "    logwood                            | 119      |
| Cutch                                | 330      | "    "    lo-kao                             | 304      |
| Cyanin                               | 7, 135   | "    "    magenta                            | 374, 377 |
| <i>Cynips folii quercus</i>          | 321      | "    "    old fustic                         | 268      |
| DARK chocolate mordant               | 75       | "    "    Persian berries                    | 274      |
| "    purple mordant                  | 73       | "    "    quercitron                         | 261      |
| "    red mordant                     | 74       | "    "    safflower                          | 138      |
| <i>Datisca cannabina</i>             | 258      | "    "    sumach                             | 326      |
|                                      |          | "    "    turmeric                           | 287      |
|                                      |          | "    "    weld                               | 278      |



|                                    | Page.    |                                    | Page. |
|------------------------------------|----------|------------------------------------|-------|
| Dyestuffs, comparison of .....     | 347      | Fustic .....                       | 262   |
| Dyewoods, red .....                | 113      | „ dyeing with old .....            | 268   |
| EFFECT of heat on colours ...      | 20       | „ old .....                        | 263   |
| Effects of salts on colours.....   | 18       | „ reactions of young.....          | 269   |
| Electricity, action of on flowers. | 10       | „ young .....                      | 268   |
| Ellagic acid .....                 | 321      | Fustin .....                       | 269   |
| Emeraldine.....                    | 414      | GALLEÏN .....                      | 318   |
| Eosin .....                        | 251      | Gallic acid .....                  | 313   |
| Erythric acid .....                | 239      | Gallin .....                       | 318   |
| Erythrin .....                     | 239      | Gallipoli oil .....                | 70    |
| Erythrite .....                    | 235, 243 | Gall-nuts.....                     | 321   |
| Erythrobenzene .....               | 372      | Gallotannic acid.....              | 311   |
| Erythrolein.....                   | 248      | Galls .....                        | 321   |
| Erythrolitmin.....                 | 248      | „ Aleppo .....                     | 322   |
| Erythromannite (erythrite).....    | 243      | „ Chinese.....                     | 323   |
| Erythrozym.....                    | 24, 25   | „ Japanese .....                   | 323   |
| Estimation of tannin.....          | 338      | Gambier .....                      | 330   |
| Ethylalizarin .....                | 43       | „ catechu.....                     | 331   |
| Ethylaniline .....                 | 398      | Gamboge.....                       | 294   |
| Ethylidiphenylamine violet .....   | 399      | „ composition of .....             | 295   |
| Ethylic orsellinate.....           | 240, 242 | „ pipe.....                        | 294   |
| Ethylorcin .....                   | 238      | <i>Gambogia gutta</i> .....        | 294   |
| Ethylrosaniline .....              | 393      | Garanceaux.....                    | 88    |
| Euxanthic acid .....               | 297      | Garancin and madder style,         |       |
| Euxanthone .....                   | 298      | difference between..               | 87    |
| Evaporation, apparatus for .....   | 147      | „ dyeing power of.....             | 86    |
| <i>Evernia prunastri</i> .....     | 245      | „ extracting, with bisul-          |       |
| „ <i>vulpina</i> .....             | 296      | phide of carbon ...                | 96    |
| Evernic acid .....                 | 245      | „ from munjeet .....               | 109   |
| Everminic acid .....               | 245      | „ manufacture of .....             | 84    |
| Examination of mordants.....       | 348      | „ oxalic acid from wash-           |       |
| Extract, alizaric .....            | 93       | ings .....                         | 86    |
| „ of brazil wood .....             | 125      | Garancine modifiée .....           | 85    |
| „ „ logwood .....                  | 119      | <i>Garcinia morella</i> .....      | 294   |
| „ „ madder, Leitenber-             |          | <i>Gardenia grandiflora</i> .....  | 301   |
| ger's ...                          | 91       | Garnet, Schultz .....              | 432   |
| „ „ „ orange.....                  | 94       | <i>Gaultheria procumbens</i> ..... | 163   |
| „ „ „ Paraf's ...                  | 92       | Geranosine .....                   | 382   |
| „ „ „ Pernod's ...                 | 95       | Goldgelb .....                     | 469   |
| „ „ „ recipes for                  |          | Gopher wood .....                  | 329   |
| dyeing with .....                  | 96       | Grain colours .....                | 221   |
| „ pectic .....                     | 94       | Grana fina .....                   | 208   |
| FAST colours .....                 | 19       | Granilla .....                     | 208   |
| Fernambuco wood.....               | 121      | Green, aldehyde... ..              | 414   |
| Flavin .....                       | 260      | „ alizarin .....                   | 93    |
| Fleurs de garance .....            | 88       | „ bladder .....                    | 305   |
| Florence lake.....                 | 128      | „ Chinese .....                    | 301   |
| Florentine lake .....              | 220      | „ crystallised .....               | 420   |
| Flowers, action of electricity on. | 10       | „ iodine .....                     | 416   |
| „ colouring matters of ...         | 7        | „ methyl.....                      | 422   |
| „ of madder .....                  | 89       | „ methylaniline.....               | 422   |
| Fluorescein.....                   | 251      | „ Perkin's .....                   | 422   |
| Fol's yellow .....                 | 468      | „ sap .....                        | 305   |
| Formation of indigo .....          | 146      | „ soluble .....                    | 420   |
| „ rosaniline .....                 | 359      | „ transformation of iodine         | 421   |
| French purple .....                | 232      | Greens, aniline .....              | 414   |
| Furfurol (foot note) .....         | 85       | „ from tertiary monamines          | 423   |
|                                    |          | Grey Casthelaz .....               | 449   |

|  | Page.    |                                     | Page.         |
|--|----------|-------------------------------------|---------------|
| Grey Laüber's .....                      | 448      | Indigo, dyeing with .....           | 196           |
| Guaiacum, action of light on ...         | 6        | „ formation of .....                | 146           |
| Gum-kino .....                           | 330      | „ from urine .....                  | 205           |
| HÆMATEATE of ammonia... 115              |          | „ manufacture .....                 | 141           |
| Hæmatein .....                           | 115      | „ printing .....                    | 185           |
| Hæmatin .....                            | 114      | „ pulverisation of .....            | 198           |
| Hæmatoxylin .....                        | 114      | „ purification of .....             | 188           |
| „ a test for lime car-                   |          | „ recovery of waste .....           | 197           |
| „ bonate .....                           | 116      | „ red .....                         | 151           |
| „ reactions of .....                     | 117      | „ reduction of, by hyposul-         |               |
| <i>Hæmatoxylon campechianum</i> 113, 118 |          | „ phites .....                      | 184           |
| Heat, action of on colouring mat-        |          | „ testing .....                     | 191           |
| ters.....                                | 11       | „ white .....                       | 182           |
| „ effect of on colours.....              | 20       | <i>Indigofera</i> .....             | 140           |
| Heavy aniline.....                       | 363      | Indigopurpurin .....                | 173           |
| Hemlock spruce..                         | 328      | Indigosulphonic acids .....         | 175           |
| „ tree .....                             | 328      | Indigotic acid.....                 | 162           |
| Hennis.....                              | 329      | Indigotin .....                     | 150, 158      |
| Hepatic aloes.....                       | 279      | „ properties of .....               | 158           |
| Hoang-tchy.....                          | 301      | „ pure .....                        | 158           |
| Hofmann gum .....                        | 398      | „ synthesis of .....                | 169, 173      |
| „ violets.....                           | 393      | Indihumin .....                     | 151, 153      |
| Huile tournante .....                    | 69       | Indin .....                         | 161           |
| Hydralizarin .....                       | 36       | Indiretin .....                     | 151, 153      |
| <i>Hydrastis canadensis</i> .....        | 294      | Indirubin .....                     | 150, 151, 155 |
| Hydride of alizarin .....                | 40       | Indol .....                         | 171           |
| „ purpurin .....                         | 59       | Indophane .....                     | 473           |
| Hydrindic acid .....                     | 170      | Injurious effects of rubiacin ..... | 81            |
| Hydroberberine .....                     | 294      | Iodine green .....                  | 416           |
| Hydrochrysammide .....                   | 284      | „ transformation of... 421          |               |
| Hydrocyanrosaniline .....                | 370      | Isalizarin.....                     | 36            |
| Hydrodiazoresorufin .....                | 250      | Isamic acid.....                    | 161           |
| Hypochlorite of soda, clearing           |          | Isamide .....                       | 162           |
| with .....                               | 84       | Isatic acid .....                   | 160           |
| Hyposulphindigotic acid .....            | 177      | Isatimide .....                     | 162           |
| Hyposulphites, reduction of in-          |          | Isatin .....                        | 159           |
| digo by .....                            | 184      | <i>Isatis indigotica</i> .....      | 144           |
| <i>ILEX aquifolium</i> .....             | 296      | „ <i>tinctoria</i> .....            | 143, 146      |
| Ilixanthin .....                         | 296      | Isatyde .....                       | 160           |
| Imasatin .....                           | 161      | Isatoflavin .....                   | 162           |
| Imesatin .....                           | 161      | Isatopurpurin .....                 | 162           |
| Indian vat .....                         | 203      | Isatosulphites .....                | 162           |
| „ yellow.....                            | 297      | Isodulcite .....                    | 256           |
| Indican .....                            | 147      | Isomorin .....                      | 266           |
| „ action of acids on .....               | 150      | Isopurpurate of potassium.....      | 457           |
| „ „ alkalis on .....                     | 155      | Isopurpuric acid.....               | 456           |
| „ „ leucin from .....                    | 151, 154 | Iso-uvitic acid.....                | 295           |
| Indicanin .....                          | 155      | JACOBSEN'S yellow .....             | 431           |
| Indifulvin .....                         | 151      | Jamaica wood.....                   | 122           |
| Indifuscin .....                         | 151      | Japanese galls.....                 | 323           |
| Indiglucin .....                         | 150, 153 | Japonic acid .....                  | 335           |
| Indigo .....                             | 140      | <i>Jateorhiza palmata</i> .....     | 293           |
| „ action of chlorine on ... 164          |          | Jola .....                          | 220           |
| „ aniline from .....                     | 169, 353 | KAMBE wood .....                    | 128           |
| „ carmine.....                           | 178, 179 | Kermes .....                        | 220           |
| „ commercial .....                       | 189      | Kino .....                          | 330           |
| „ dyeing cotton with .....               | 199      | Knoppers .....                      | 323           |



|                                   | Page.         |                                      | Page.    |
|-----------------------------------|---------------|--------------------------------------|----------|
| Kopp's alizaric extract .....     | 93            | Madder .....                         | 22       |
| „ green alizarin.....             | 93            | „ adulteration of .....              | 104      |
| „ purpurin.....                   | 92            | „ alcohol from.....                  | 89       |
| „ violet .....                    | 392           | „ changed by keeping.....            | 26       |
| Kuphaniline .....                 | 363           | „ colours on cloth .....             | 107      |
| Kyanol .....                      | 352           | „ composition of .....               | 24       |
| LAC .....                         | 222           | „ dyeing .....                       | 81       |
| „ dye .....                       | 222, 224      | „ „ clearing .....                   | 83       |
| „ lake.....                       | 224           | „ „ soaping.....                     | 83       |
| Lacmus .....                      | 248           | „ „ use of chalk in, 27, 81          |          |
| Lake, Berlin .....                | 128           | „ extract, recipes for dye-          |          |
| „ Florence .....                  | 128           | ing with .....                       | 96       |
| „ Florentine .....                | 220           | „ extracts of.....                   | 90       |
| „ madder .....                    | 103           | „ flowers of .....                   | 89       |
| „ Venetian .....                  | 128           | „ injured by keeping .....           | 89       |
| Lakes, carmine .....              | 218           | „ lake .....                         | 103      |
| <i>Lawsonia inermis</i> .....     | 329           | „ manufacture of.....                | 23       |
| <i>Lecanora tartarea</i> .....    | 229, 241, 247 | „ sugar from .....                   | 35       |
| Lecanoric acid .....              | 240           | „ testing .....                      | 105      |
| Lecanorin .....                   | 241           | „ use of .....                       | 64       |
| Leitenberger's extract of madder  | 91            | Magdala red .....                    | 478      |
| Leucaniline.....                  | 370           | Magenta .....                        | 363      |
| Leuch's vat .....                 | 204           | „ adulteration of .....              | 379      |
| Leucin from indican .....         | 151, 154      | „ discovery of .....                 | 364      |
| Leukaurin .....                   | 467           | „ dyeing with .....                  | 374, 377 |
| Lichen, wall .....                | 296           | „ manufacture of..                   | 365, 373 |
| Lichens .....                     | 228, 296      | „ printing with ...                  | 377, 378 |
| „ testing .....                   | 233           | „ purification of .....              | 367      |
| Light, analysis of .....          | 2             | Manchester yellow .....              | 472      |
| „ aniline .....                   | 363           | Manganese mordant for aniline        |          |
| „ chocolate mordant.....          | 75            | black .....                          | 439      |
| „ oil.....                        | 352           | Manufacture of aniline .....         | 356      |
| „ purple mordant .....            | 73            | „ Bleu de Lyon ...                   | 403      |
| „ red mordant.....                | 74            | „ garancin .....                     | 84       |
| Lightfoot's experiments with ani- |               | „ indigo .....                       | 141      |
| line black .....                  | 443           | „ madder .....                       | 23       |
| „ process.....                    | 186           | „ magenta ...                        | 365, 373 |
| Lima wood.....                    | 122           | „ mauve.....                         | 385, 388 |
| Litmus.....                       | 248           | „ nitrobenzene ...                   | 355      |
| Liver aloes .....                 | 279           | „ orchil .....                       | 229      |
| Lloyd Dale's process.....         | 401           | „ rosaniline.....                    | 371      |
| Logwood.....                      | 113           | Maroons, aniline .....               | 432      |
| „ black .....                     | 120           | Martius' yellow .....                | 472      |
| „ dyeing with.....                | 119           | Mauve, discovery of .....            | 384      |
| „ extract.....                    | 119           | „ manufacture of .....               | 385, 388 |
| „ preparation of for dye-         |               | „ purification of .....              | 385      |
| ing .....                         | 118           | Mauvaniline .....                    | 367, 392 |
| „ purple .....                    | 120           | Mauveine .....                       | 386      |
| Lokaetin .....                    | 304           | Melin .....                          | 274      |
| Lokain.....                       | 302           | <i>Menispermum fenestratum</i> ..... | 293      |
| Lo-kao.....                       | 301           | Mestèque .....                       | 208      |
| „ dyeing with.....                | 304           | Meta-amidobenzoic acid .....         | 167      |
| Loose colours .....               | 19            | Metagallic acid .....                | 312, 317 |
| Luteolin .....                    | 277           | Metanitrotoluene .....               | 361      |
| MACHROMIN .....                   | 265           | Metatoluidine.....                   | 362      |
| <i>Maclura tinctoria</i> .....    | 262           | Methyl green .....                   | 422      |
| Maclurin .....                    | 264           | „ salicylate .....                   | 163      |
|                                   |               | Methylaniline.....                   | 397, 398 |
|                                   |               | „ green .....                        | 422      |



|                                   | Page.    |                                    | Page.    |
|-----------------------------------|----------|------------------------------------|----------|
| Methylorcin .....                 | 238      | Nitrobenzene, manufacture of ...   | 355      |
| Methylrosanilines .....           | 393      | Nitrococcusic acid .....           | 213      |
| Mimotannic acid .....             | 333      | Nitrocinnamic acid.....            | 172      |
| Mimotanninhydroetin .....         | 336      | Nitroerythrite.....                | 244      |
| Mock Turkey red .....             | 131      | Nitro-orcins .....                 | 236, 237 |
| Mononitro-orcin .....             | 237      | Nitronaphthalene .....             | 476      |
| Monophenylrosaniline .....        | 390      | Nitronaphthalic acid .....         | 475      |
| Monoxanthraquinone .....          | 46       | Nitrophloroglucin .....            | 259      |
| Mordant, black .....              | 75       | Nitropurpurin.....                 | 41       |
| "    dark chocolate .....         | 75       | Nitrosalicylic acid .....          | 162      |
| "    "    purple .....            | 73       | Nitrotoluenes .....                | 360      |
| "    "    red.....                | 74       | Nopal .....                        | 206      |
| "    light chocolate .....        | 75       | Nucitannin .....                   | 329      |
| "    "    purple .....            | 73       |                                    |          |
| "    "    red.....                | 74       | OAK bark .....                     | 328      |
| Mordanting Turkey red.....        | 67       | Ænolin .....                       | 135      |
| Mordants, examination of.....     | 348      | Oil, Gallipoli.....                | 70       |
| "    printing machine for .....   | 76       | "    of wintergreen .....          | 163      |
| "    theory of .....              | 17       | Oiling Turkey red.....             | 66       |
| "    Thom's experiments .....     | 17       | Old fustic .....                   | 263      |
| on.....                           | 17       | "    dyeing with .....             | 268      |
| Moric acid .....                  | 264, 266 | "    reactions of .....            | 263      |
| Morin .....                       | 266      | Optical characters of alizarin ... | 62       |
| "    blanc .....                  | 263      | "    "    purpurin..               | 60       |
| "    jaune .....                  | 263      | Orange extract of madder .....     | 94       |
| "    relation of to rhamnetin ... | 273      | Orcein.....                        | 237      |
| <i>Morinda citrifolia</i> .....   | 111      | Orchil .....                       | 228      |
| Morindin .....                    | 111      | "    manufacture of .....          | 229      |
| Morindone .....                   | 111      | "    uses of .....                 | 233      |
| Morintannic acid .....            | 264      | Orcin .....                        | 234      |
| <i>Morus tinctoria</i> .....      | 262      | Orellin .....                      | 290      |
| Munjeet .....                     | 106, 108 | Orsellesic acid .....              | 246      |
| "    garancin .....               | 109      | Orsellic acid .....                | 241, 243 |
| Mungistin .....                   | 109      | Orsellinic acid .....              | 246      |
| Murexide .....                    | 225, 457 | Orthonitrotoluene .....            | 361      |
| Myrobalans .....                  | 328      | Orthotoluidine .....               | 362      |
|                                   |          | Oxalic acid from garancin wash-    |          |
| NAPHTHA, coal-tar .....           | 352      | ings .....                         | 86       |
| Naphthalene .....                 | 470      | Oxindicanin .....                  | 157      |
| "    colours .....                | 470      | Oxindol .....                      | 171      |
| Naphthalenesulphonic acid .....   | 471      | Oxynaphthalic acid .....           | 56       |
| Naphthazarin .....                | 55       | Oxyphenic acid .....               | 336      |
| Naphthol.....                     | 471      | Oxytoluic acid .....               | 360      |
| Naphthylamine .....               | 475      |                                    |          |
| "    red.....                     | 478      | PALUDS .....                       | 24       |
| "    violet.....                  | 480      | Paracarthamin .....                | 299      |
| Naphthylpurpuric acid .....       | 473      | Paracoumaric acid.....             | 282      |
| Natal aloes .....                 | 279      | Paradatisetin.....                 | 257, 258 |
| Nataloin .....                    | 281      | Paraf's extract of madder.....     | 92       |
| Nature of aniline black.....      | 442      | Paranitrotoluene .....             | 360      |
| "    colouring matters.....       | 3        | Paraoxybenzoic acid .....          | 282      |
| Neb-neb .....                     | 327      | Pararosaniline .....               | 374      |
| Nicholson's blue.....             | 407      | Paratoluidine .....                | 362      |
| Night blue .....                  | 404      | Parellic acid .....                | 247      |
| Nigraniline .....                 | 444      | Paris violet.....                  | 397      |
| Nitrindin .....                   | 161      | <i>Parmelia parietina</i> .....    | 296      |
| Nitroacetophenone.....            | 169      | Pastel .....                       | 143      |
| Nitroalizarin .....               | 41       | Peach wood .....                   | 121      |
| Nitrobenzene .....                | 354      | Pectic extract.....                | 94       |

|   | Page.         |  | Page.       |
|---|---------------|--|-------------|
| Peonine .....                               | 462           | Purification of mauve .....                  | 385         |
| Perchlorquinone .....                       | 166           | Purple assistant liquor .....                | 73          |
| Perkin's green .....                        | 422           | „ logwood .....                              | 120         |
| Pernambuco wood.....                        | 121           | „ mordant dark.....                          | 73          |
| Pernod's extract of madder .....            | 95            | „ „ light .....                              | 73          |
| Persian berries .....                       | 270           | „ Regina .....                               | 391         |
| „ „ dyeing with.....                        | 274           | Purpurin.....                                | 38, 58, 110 |
| „ „ reactions of.....                       | 270           | „ hydrate .....                              | 37          |
| Phenicienne .....                           | 468           | „ hydride of .....                           | 59          |
| Phenol .....                                | 450           | „ detection of .....                         | 63          |
| Phenylcarbamic acid .....                   | 167           | „ Kopp's .....                               | 92          |
| Phenyl violets .....                        | 391           | „ optical characters of.....                 | 60          |
| Phloramine .....                            | 259           | Purpurinamide .....                          | 58          |
| Phloroglucin .....                          | 257, 259, 264 | Purpurolein .....                            | 134         |
| Phoenicine .....                            | 387           | Purpuroxanthin .....                         | 37, 38      |
| Phosphine .....                             | 425           | Purree .....                                 | 297         |
| Phyllocyanin .....                          | 307           | Pyrocatechin .....                           | 336         |
| Phylloxanthin .....                         | 307           | Pyrocatechuic acid.....                      | 336         |
| Picramic acid.....                          | 456           | Pyrogallic acid .....                        | 316         |
| Picric acid .....                           | 163, 452      | Pyrogallol .....                             | 316         |
| Picrocyamic acid .....                      | 456           |  |             |
| Picroerythrin .....                         | 240, 242, 246 | QUERCETIC ACID .....                         | 257, 258    |
| Pincoffine .....                            | 88            | Quercetin.....                               | 255, 259    |
| Pipe gamboge .....                          | 294           | Quercimeric acid .....                       | 258         |
| <i>Podophyllum peltatum</i> .....           | 294           | Quercitannic acid .....                      | 255, 328    |
| Podyophyllum root .....                     | 294           | Quercitrin .....                             | 255         |
| Pollution of rivers .....                   | 85            | Quercitron .....                             | 253         |
| <i>Polygonum fagopyrum</i> .....            | 296           | „ dyeing with .....                          | 261         |
| „ <i>tinctorium</i> .....                   | 144           | „ reactions of .....                         | 254         |
| Pomona paste.....                           | 424           | <i>Quercus ægylops</i> .....                 | 324         |
| Ponceau .....                               | 382           | „ <i>infectoria</i> .....                    | 321         |
| Potassium isopurpurate.....                 | 457           | „ <i>nigra</i> .....                         | 253         |
| Preparation of cochineal .....              | 208           | „ <i>robur</i> .....                         | 323         |
| „ „ logwood for dyeing .....                | 118           | „ <i>tinctoria</i> .....                     | 253         |
| „ „ woad .....                              | 143           |  |             |
| Printing calico.....                        | 72            | REACTIONS of annatto.....                    | 289         |
| „ chlorophyll .....                         | 309           | „ barwood .....                              | 132         |
| „ indigo .....                              | 185           | „ brazil wood ex-                            |             |
| „ machine for mordants ..                   | 76            | tract .....                                  | 125         |
| „ Turkey red .....                          | 71            | „ catechu .....                              | 332         |
| „ with artificial alizarin... 100           |               | „ cochineal .....                            | 213         |
| „ „ magenta.....                            | 377, 378      | „ hæmatoxylin... 117                         |             |
| „ „ safranine .....                         | 381           | „ old fustic .....                           | 263         |
| Process of Lloyd Dale.....                  | 401           | „ Persian berries .....                      | 270         |
| Properties of indigotin .....               | 158           | „ quercitron.....                            | 254         |
| Protocatechuic acid ... 258, 264,           | 335           | „ sandal wood... 132                         |             |
| <i>Protococcus vulgaris</i> .....           | 244           | „ sumach .....                               | 352         |
| Pseudo-corallin .....                       | 465           | „ weld .....                                 | 276         |
| Pseudo-curcumin .....                       | 286           | „ young fustic ... 269                       |             |
| Pseudo-erythrin (ethylic orsellinate) ..... | 240           | Recipes for dyeing with madder extract ..... | 96          |
| Pseudo-orcin (erythrite) .....              | 243           | Recovery of waste colour ... 101,            | 102         |
| Pseudo-purpurin .....                       | 36, 38        | „ „ indigo .....                             | 197         |
| <i>Pterocarpus marsupium</i> .....          | 330           | Red Adrianople.....                          | 64          |
| „ <i>santalinus</i> .....                   | 128           | „ corallin ...                               | 462         |
| Pulverising indigo .....                    | 198           | „ dyewoods .....                             | 113         |
| Pure indigotin .....                        | 158           | „ Magdala.....                               | 478         |
| Purification of indigo .....                | 188           | „ mordant dark.....                          | 74          |
| „ „ magenta .....                           | 367           | „ „ light .....                              | 74          |



|                                  | Page.         |                                    | Page.    |
|----------------------------------|---------------|------------------------------------|----------|
| Red naphthylamine .....          | 478           | Rubichloric acid.....              | 29       |
| „ Turkey .....                   | 64            | Rubinic acid .....                 | 335      |
| „ „ printing.....                | 71            | Rubiretin .....                    | 30, 33   |
| Reduction of indigo by hyposul-  |               | Ruficoccin .....                   | 213      |
| phites .....                     | 184           | Rufigallic acid .....              | 315      |
| Regianic acid.....               | 329           | Rufimoric acid .....               | 265      |
| Regianin.....                    | 329           | Rufitannic acid .....              | 313      |
| Regina purple .....              | 391           | <i>Rumex obtusifolius</i> .....    | 298      |
| Relation of morin and rhamnetin  | 273           | Runge's blue .....                 | 388      |
| <i>Reseda luteola</i> .....      | 276           | Rutin .....                        | 274, 298 |
| Reserve process (indigo) .....   | 200           |                                    |          |
| Resist process „ .....           | 200           | Safflower .....                    | 135      |
| Resorcin .....                   | 249           | „ composition of .....             | 136      |
| „ from sapan wood.....           | 123           | „ dyeing with .....                | 138      |
| „ indophane .....                | 473           | „ yellow colouring matter          |          |
| Rhamnagin.....                   | 272           | from.....                          | 138      |
| Rhamnetin.....                   | 272           | Saffron.....                       | 292      |
| „ relation to morin.....         | 273           | Saffronin (from saffron).....      | 292      |
| Rhamnin .....                    | 273           | Safranine or saffranine .....      | 380      |
| <i>Rhamnus catharticus</i> ..... | 302, 305      | „ hydrochloride.....               | 380      |
| Rheum .....                      | 298           | „ printing with .....              | 381      |
| Rhotic acid.....                 | 329           | Salicylic acid .....               | 163      |
| Rhubarb.....                     | 298           | Salts, effects of on colours ..... | 18       |
| <i>Rhus coriaria</i> .....       | 324           | Sandal wood .....                  | 128      |
| „ <i>cotinus</i> .....           | 268           | „ „ reactions of .....             | 132      |
| „ <i>semialata</i> .....         | 324           | Sanders wood.....                  | 128      |
| Rivers, pollution of .....       | 85            | Santa Martha wood .....            | 121      |
| Robinin .....                    | 256           | Santal .....                       | 130      |
| <i>Rocella fuciformis</i> .....  | 229, 239      | Santal wood .....                  | 128      |
| „ <i>tinctoria</i> .....         | 229, 241, 247 | Santalal acid .....                | 129      |
| Roccellic acid .....             | 247           | Santalal .....                     | 129, 130 |
| Roccellinin.....                 | 247           | Sap green .....                    | 305      |
| Rosanaphthylamine .....          | 478           | Sapan wood .....                   | 122      |
| Rosaniline .....                 | 368           | Sappanin.....                      | 123      |
| „ acetate .....                  | 369, 371      | Saxony blue .....                  | 178      |
| „ formation of.....              | 359           | Scarlet, Ulrich's .....            | 383      |
| „ hydrochloride .....            | 369           | Schützenberger's and Lalande's     |          |
| „ manufacture of.....            | 371           | process .....                      | 184      |
| „ picrate .....                  | 369           | Scoparin .....                     | 299      |
| Rose colour, brazil wood.....    | 127           | Seed-lac .....                     | 223      |
| Rosées .....                     | 24            | Sesam oil.....                     | 111      |
| Roseine .....                    | 371           | Shell-lac .....                    | 224      |
| Rosocyanin.....                  | 287           | „ composition of .....             | 224      |
| Rosolic acid .....               | 458           | Soap waste, utilisation of .....   | 103      |
| Rosotoluidine.....               | 373           | Soaping madder dyed goods .....    | 83       |
| Rothine .....                    | 468           | Socaloin .....                     | 281      |
| <i>Rottlera tinctoria</i> .....  | 301           | Socotrin aloes.....                | 279      |
| Rottlerin .....                  | 281, 301      | Soluble green.....                 | 420      |
| Ruberythric acid .....           | 35            | Sooranjee .....                    | 111      |
| Rubiatic acid .....              | 30, 33        | <i>Sophora japonica</i> .....      | 299, 304 |
| Rubiacin .....                   | 33, 34        | Sorgho.....                        | 133      |
| „ injurious effect of .....      | 81            | „ carmine .....                    | 134      |
| Rubiadin .....                   | 30, 33        | „ red .....                        | 134      |
| Rubiafin.....                    | 30, 33        | <i>Sorghum saccharatum</i> .....   | 133      |
| Rubiagin.....                    | 31            | Spaniolitmin .....                 | 248      |
| Rubian.....                      | 24, 28        | <i>Spartium scoparium</i> .....    | 299      |
| „ decomposition of.....          | 29            | Spectroscopic examination of       |          |
| Rubianic acid.....               | 36            | colours .....                      | 346      |
| Rubianin .....                   | 30, 33        | Spectrum .....                     | 2        |



|                                 | Page.    |                                  | Page.    |
|---------------------------------|----------|----------------------------------|----------|
| Spruce bark .....               | 328      | Trinitro-orcein.....             | 236      |
| Stick-lac .....                 | 222      | Trinitrophenol .....             | 452      |
| „ composition of .....          | 222      | Trinitroresorcin .....           | 123      |
| Styphnic acid.....              | 123      | Triphenylrosaniline .....        | 404      |
| Sugar from madder .....         | 35       | Triphenylrosanilinesulphonic     |          |
| „ cane, Chinese.....            | 133      | acid .....                       | 417      |
| Sulphindigotic acid .....       | 176      | Turkey red .....                 | 64       |
| Sulphisatyde .....              | 161      | „ clearing .....                 | 68       |
| Sulphoflavic acid .....         | 181      | „ dyeing.....                    | 67       |
| Sulphonaphthalic acid .....     | 471      | „ mock .....                     | 131      |
| Sulphopurpuric acid .....       | 175, 181 | „ mordanting.....                | 67       |
| Sulphorufic acid .....          | 181      | „ oiling .....                   | 66       |
| Sulphoviridic acid.....         | 180      | „ print .....                    | 71       |
| Sulphurous acid, bleaching      |          | Turmeric.....                    | 284      |
| tion of .....                   | 16       | „ dyeing with .....              | 287      |
| Sumach .....                    | 324      | „ composition of .....           | 285      |
| „ dyeing with .....             | 326      | Tyrosine .....                   | 210      |
| „ reactions of .....            | 325      |                                  |          |
| „ uses of .....                 | 326      | ULRICH'S scarlet .....           | 383      |
| Synthesis of indigo .....       | 169, 173 | <i>Uncaria gambir</i> .....      | 330      |
|                                 |          | Uric acid.....                   | 225      |
| TAIGU wood .....                | 300      | Urine, indigo from.....          | 205      |
| Taiguic acid .....              | 300      | Use of chalk in madder dyeing..  | 81       |
| Tannic acid .....               | 311      | „ madder .....                   | 64       |
| Tannin, estimation of .....     | 338      | Uses of annatto.....             | 291      |
| „ matters.....                  | 310      | „ orchil .....                   | 233      |
| Tannins .....                   | 310      | „ sumach .....                   | 326      |
| Tannoxylic acid.....            | 313      | <i>Usnea florida</i> .....       | 244      |
| Tayegu wood.....                | 300      | Usnic acid .....                 | 244      |
| Tein-hoa-tein-ching .....       | 144      | Utilisation of soap waste .....  | 103      |
| <i>Terminalia chebula</i> ..... | 328      |                                  |          |
| Terra firma wood .....          | 122      | VALONIA .....                    | 324      |
| Terra japonica .....            | 330      | <i>Variolaria dealbata</i> ..... | 229      |
| Testing cochineal .....         | 215      | „ <i>orcina</i> .....            | 229, 240 |
| „ indigo .....                  | 191      | Vat, Cohen's (indigo) .....      | 199      |
| „ lichens .....                 | 233      | „ cold (indigo) .....            | 197      |
| „ madder.....                   | 105      | „ Indian (indigo).....           | 203      |
| Theory of mordants .....        | 17       | „ Leuch's (indigo) .....         | 204      |
| Thom's experiments on mordants  | 17       | „ woad .....                     | 203      |
| Tetrabromofluorescein .....     | 251      | Venetian lake.....               | 128      |
| Tetranitroerythrite .....       | 244      | Verantin .....                   | 30, 32   |
| Tetrazoresorcin .....           | 251      | Vert-Azof .....                  | 301      |
| Tetrazoresorufin .....          | 251      | „ lumière .....                  | 301      |
| Toluene .....                   | 359      | „ Venus.....                     | 301      |
| Toluidine, blue .....           | 408      | Victoria yellow .....            | 469      |
| „ red .....                     | 373      | Violaniline .....                | 367, 392 |
| Toluidines .....                | 362      | Violet, aldehyde.....            | 400      |
| Tournesol en drapeaux.....      | 249      | „ Britannia .....                | 400      |
| Transformation of iodine green  | 421      | „ Dorothea .....                 | 398      |
| Triamylorcin .....              | 239      | „ ethyldiphenylamine .....       | 399      |
| Tribromomoric acid .....        | 266      | „ Imperial.....                  | 390      |
| Trichloraniline .....           | 164      | „ Kopp's .....                   | 392      |
| Trichlorophenol.....            | 164      | „ naphthylamine .....            | 480      |
| Triethylorcin .....             | 239      | „ Paris .....                    | 397      |
| Triethylrosaniline .....        | 393      | „ Wanklyn's.....                 | 400      |
| Trimethylchrysotoluidine.....   | 429      | Violets, aniline .....           | 384      |
| Trimethylorcin .....            | 239      | „ benzylic .....                 | 399      |
| Trimethylrosaniline, dimethyl-  |          | „ Hofmann .....                  | 393      |
| iodide of.....                  | 416, 421 | „ Phenyl .....                   | 391      |

# INDEX.

509

|                                      | Page.         |                              | Page. |
|--------------------------------------|---------------|------------------------------|-------|
| Vulpic acid .....                    | 296, 297      | Xylochloric acid .....       | 309   |
| WAIFA.....                           | 274, 299, 304 | YELLOW, adulteration of ani- |       |
| Wall lichen.....                     | 296           | line.....                    | 431   |
| Walnut husks.....                    | 329           | ,, alizarin.....             | 93    |
| Wanklyn's violet .....               | 400           | ,, bark .....                | 293   |
| Waste colour, recovery of...101, 102 |               | ,, Campo Bello .....         | 469   |
| ,, indigo, recovery of .....         | 197           | ,, colouring matter          |       |
| ,, utilisation of soap .....         | 103           | from flowers ...             | 138   |
| Weld .....                           | 276           | ,, corallin.....             | 466   |
| ,, dyeing with .....                 | 278           | ,, Dutch .....               | 275   |
| ,, reactions of .....                | 276           | ,, Fol's.....                | 468   |
| White indigo .....                   | 182           | ,, Indian .....              | 297   |
| ,, light, analysis of.....           | 2             | ,, Jacobsen's .....          | 431   |
| Woad .....                           | 143, 146      | ,, Manchester .....          | 472   |
| ,, preparation of .....              | 143           | ,, Martius' .....            | 472   |
| ,, vat .....                         | 203           | ,, Victoria .....            | 469   |
| Wongshy .....                        | 301           | ,, wood .....                | 263   |
| Wintergreen oil.....                 | 163           | Yellows, aniline.....        | 425   |
| XANTHEIN .....                       | 9             | Young fustic .....           | 268   |
| Xanthin.....                         | 25, 28, 29    | ,, reactions of.....         | 269   |
| ,, of flowers.....                   | 8             | ZACATILLA .....              | 208   |
| Xantholein.....                      | 134           | Zanzibar aloes .....         | 279   |
| Xanthorhammin .....                  | 271, 272      | Zinaline .....               | 430   |
| Xylidine red .....                   | 374           |                              |       |

## ERRATA.

Page 24, line 9, for 'palus,' read 'palud.'

„ 88, „ 11, „ 'or clearing,' read 'but only clearing.'

„ 127, „ 9, „ 'M. K. Koechlin,' read 'M. H. Koechlin.'

„ 166, „ 30, „ 'Bromisatinic acid,' read 'Bromisatic acid.'

„ 166, „ 32, „ 'Dibromisatinic acid,' read 'Dibromisatic acid.'

„ 227, „ 10, „ '*poupre*,' read '*pourpre*.'

„ 229, „ 17, „ '*Leconaria*,' read '*Lecanora*.'

„ 236, „ 13-14, „ 'monobromicin,' read 'monobromorcin.'

„ 294, „ 15, „ '*hydroberberin*,' read '*hydroberberine*.'

„ 301, „ 27, „ '*Vert-lumiere*,' read '*Vert-lumière*.'

„ 456, „ 6, „ ' $2\text{OH}$ ,' read ' $2\text{OH}_2$ .'



JUST PUBLISHED,

In Two Handsome Quarto Volumes, strongly Bound, containing 40 Plates,  
and 259 other Illustrations.

PRICE £4 4s.

THE SCIENCE OF  
MODERN COTTON SPINNING.

BY

EVAN LEIGH, C.E.

*Palmer & Howe, Publishers, 1, 3, and 5, Bond Street, Manchester.*

*Simpkin, Marshall, & Co., London.*

---

OPINIONS OF THE PRESS.

---

[*From the* MANCHESTER EXAMINER AND TIMES.]

Cotton spinning is not often honoured by being the subject of such handsome volumes as these, but Mr. Leigh evidently thought the history of cotton, from its growth in America or India to its appearance as twist, was not only worthy of a detailed record, but of a work in which neither the engraver's nor the printer's art should leave anything to be desired. Accordingly we have two folio volumes which rival in appearance most of the illustrated gift books of the season, printed on fine paper, and illustrated by a considerable number of engravings.

But if the first sight of the work should suggest the idea of its purpose being merely to provide scientific entertainment for the drawing room, the impression would be erroneous; the work is essentially practical, and though a knowledge of cotton spinning is not often acquired by the study of books, we may add that Mr. Leigh's book is pre-eminently didactic. The first edition, indeed, was so successful that, we understand, arrangements have already been made for translations of the book into several foreign languages.

Throughout the book, as we stated above, Mr. Leigh is very practical, and his advice is the result of considerable personal experience during nearly half a century. But we will leave others better acquainted with the subject to say how far he is justified in making the inferential promise in the following passage from the preface:—"The author dwells but little on present examples, which may be seen in every day operation, but rather points to the inevitable future, taking care to advise no step but what is both safe and practical, and by which large sums of money may be saved in original outlay, and consequently in cost of production." But many spinners who are at a loss for advice when about to make changes in machinery, &c., may turn with advantage to Mr. Leigh's book as an impartial guide, the object of which is to counsel real economy, and to give recommendations without favour.

In a work of this character the author, of course, trusts very much to the assistance of his engraver, and Mr. Leigh in this respect is extremely fortunate. The engravings tell their own story, and, so far as this department is concerned, the book is almost exhaustive.

[From the MANCHESTER GUARDIAN.]

These handsome volumes mark a decided advance upon anything in the literature of cotton spinning which, so far as our acquaintance goes, has yet been published in this country. The author, who has had nearly half a century's extended and active experience in the business, ought certainly to have something to say worth the attention of all who have more recently entered it, and even of others who, though not inexperienced, have had a few opportunities of wide observation. A book of this kind has, in fact, for some time back been wanted. Most of those previously extant are out of date, and little has been hitherto done toward collecting together the scattered results of improvements in machinery and in methods of management which little by little have wrought on the whole no inconsiderable changes in the operations of cotton spinning.

The first part of the book supplies a very full description of the principal varieties of cotton, together with a statistical account of their production. Then comes a chapter on mill architecture, which includes some lengthened observations upon building materials. On the question of "belting *versus* mill gearing" English spinners will scarcely be at first sight disposed to side with Mr. Leigh in his decided preference for belting. Yet this plan appears to be almost universally adopted in America. There certainly appears much to be said in its favour, and perhaps the high cost of iron now prevailing may lead to a trial of the system in this country ere long.

Some pages on steam engines complete what may be called the introductory part of the work, and we now enter upon the earlier stages of the process of cotton spinning proper—viz., mixing, opening, and scutching. Besides the older forms of openers and scutchers, the more recent ones of Crighton and Lord are very fairly described. On the subject of carding Mr. Leigh gives his opinion at once in favour of "flats" as against rollers.

In connection with this subject we have also much very valuable information respecting the choice and management of cards. Some pages are devoted to the combing machine, not only the beautiful and well-known invention of Heilmann, but also a more recent discovery of Joseph Imbs, who, like the late M. Heilmann, is a native of France. In the remarks on slubbing, intermediate and roving frames we have much useful practical advice respecting the adjustment of draughts and the management of these preparatory processes.

Passing on now to the chapters on spinning, we have, after a judiciously slight historical sketch, a full and interesting account of the throstle frame in all its varieties. Mule spinning receives equally full treatment, and then follow very useful directions for doubling, gassing, polishing, and spooling.

The illustrations are abundant, and the mechanical drawing is very well done. We repeat, in conclusion, our opinion that this is the best work on the subject of cotton spinning that has yet appeared in this country.

[From the MANCHESTER COURIER.]

An examination of the two handsome volumes before us will show that the promise of the title, lengthy though it be, is more than fulfilled. The articles are most elaborate, and most carefully written, while so far as we can discover the most perfect impartiality is exhibited with reference to the machinery described. The introductory chapter describes the varieties of the cotton plant and illustrates most completely the length of staple of the different kinds by means of illustrations of full size laid out on a scale of tenths of an inch. Then comes a chapter on cotton mill architecture, with an account of the great "India Mill" at Over Darwen, the architect's plans, sections, and elevations of which are fully given.

The remaining chapters will be found equally useful and equally practical, and if Mr. Leigh's work as a whole cannot pretend to any special graces of style or remarkable literary merit, it may at least be said that he has brought to his task great practical knowledge and abundant common sense.











[illegible]

MAY 10

1-2536



667.3

C137 D

4738

SPECIAL

87-B

16534

THE GETTY CENTER  
LIBRARY



